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**SYLLABUS OF DENTAL MATERIALS**

1984



**LTC(P) GERALD D. WOOLSEY, D.D.S., M.S.**

**CHIEF, DENTAL MATERIALS BRANCH**

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of restorative materials can be experienced. For example, the widespread use of high copper amalgams in the military was not evidenced until the early 1980's (Caulk Optalloy, with a high gamma<sub>2</sub> phase content, was the most commonly used amalgam. A tremendous publicity "blitz" by dental manufacturers is underway to convince the dental profession that posterior composite restorative materials are "as durable as amalgam restorations." Current dental research does not support this belief. Agar hydrocolloid and rubber base impression materials are the most commonly used dental impression materials in the military today; there are improvements in both techniques which can conserve resources while yielding excellent reproductions of prepared teeth.

The continuing goal of this work is an annual update of the information, lists of materials and devices, and dissemination of this information to those most in need--the practicing military dental residents and clinicians.

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**SYLLABUS OF DENTAL MATERIALS**

*by*

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**UNITED STATES ARMY INSTITUTE OF DENTAL RESEARCH**



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FOREWORD

Investigation into the physical properties, handling characteristics, storage stability, and cost effectiveness of dental materials has consumed, and will continue to consume, a considerable amount of personnel time and monetary resources at our United States Army Institute of Dental Research. This research is for naught if it is not promulgated. Accordingly, I have directed that this syllabus be written, published, and distributed in order to fill the information gap between the beginning of actual research and textbook-style publication. A yearly update will continue to be published and the new information can be added to your syllabus.

The data contained herein have been painstakingly compiled by LTC (P) Gerald D. Woolsey, DC and CAPT Joseph P. Moffa with help from COL James E. Overberger, USAR. The spirit of "Research for the Soldier" (don't forget we are also soldiers) has been captured by this eclectic group of scientists - an active-duty Army Officer, an active-duty Public Health Officer, and an Army Reserve Dental Officer. They have done an extraordinary job for which I offer my thanks.

THOMAS P. SWEENEY  
Colonel, Dental Corps  
Commanding

10 July 1984

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## PREFACE

↳ This syllabus <sup>was</sup> has been prepared for military dental residents and clinicians. <sup>It</sup> It is not our intent to cover all aspects of dental materials science, but to presents a simplified review of the current status of modern restorative materials and devices, and offers alternative techniques, and examples of materials and devices which might improve the quality of military dental care by diminishing expense, and conserving resources.

As new materials appear upon the dental market and the military dentist is subjected to advertising claims, considerable misunderstanding of the proper use of restorative materials can be experienced. For example, the widespread use of high copper amalgams in the military was not evidenced until the early 1980s (Caulk Optalloy, with a high gamma<sub>2</sub> phase content, was the most commonly used amalgam). A tremendous publicity blitz by dental manufacturers is underway to convince the dental profession that posterior composite restorative materials are "as durable as amalgam restorations". Current dental research does not support this belief. Agar hydrocolloid and rubber base impression materials are the most commonly used dental impression materials in the military today; there are improvements in both techniques which can conserve resources while yielding excellent reproductions of prepared teeth. *Original - suggested keywords include: (→ top 10/73 A)*

The continuing goal of this work is an annual update of the information, lists of materials and devices, and dissemination of this information to those most in need--the practicing military dental residents and clinicians.

Information, questions, and suggestions relative to future revisions can be submitted to this address.

COMMANDER, USAIDR  
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If this work can improve the quality of military dental care in any measurable amount, the syllabus will have been worth the effort.

GDW

## ACKNOWLEDGMENTS

This work would not have been possible  
without the help of many people.

Without the support and encouragement of Thomas P. Sweeney Colonel, Dental Corps (Commander, USAIDR), none of this work could have been realized. His task has not been an easy one, he has maintained a cheerful spirit in the midst of sorrowful moments and bitter disappointments. From his positive example, we might all learn.

Dr. Joseph P. Moffa (Chief, Clinical Research Branch, USAIDR) who has been my colleague and friend for the past year, not only provided the chapter "Dental Casting Alloys", but, helped to proof and assemble this document in its final form.

Lottie Applewhite provided considerable help with the numerous editorial revisions by providing suggestions for the style of the syllabus. Her depth of understanding in all of these areas is a wonderful resource.

I wish to express appreciation to Dr. James Overberger, Colonel, Dental Corps/USAR for his suggestions about the first three chapters.

Grace Nonomura was helpful in typing two chapters and proofing the document; I appreciate her aid. I am grateful to Kris T. Jurado for her help in composing the cover, flypage, titles, and subtitles; this helped give the syllabus a touch of class.

Gerald D. Woolsey, DDS, MS  
LTC(P), Dental Corps



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## CHAPTER I

### PROPERTIES OF DENTAL MATERIALS

Dental materials can be characterized by physical and mechanical properties. Physical properties are directly related to the type of molecules and bonding present. Mechanical properties are dependent upon the type of molecules and bonding as well as the size, shape, and crystalline structure of the material (1).

This chapter includes information on the physical properties of dental materials; bonding, optical properties, corrosion, surface phenomena, and thermal expansion. Mechanical properties of dental materials are discussed in terms of strength, stress and strain, viscosity, creep, viscoelasticity, modulus of elasticity, and hardness.

#### PHYSICAL PROPERTIES

##### Bonding

Primary bonding is of three types--ionic, covalent, and metallic. Ionic bonding occurs between metallic and nonmetallic elements, and involves an electron exchange between ions. Materials bonded ionically are good insulators as solids, and conductors as liquids. At room temperature, they are brittle materials. Ionic bonding is found in porcelain, glasses, and some crystals like quartz. Covalent bonds occur between polar molecules and are the strongest of all bonds. Covalent bonds are found in materials which share electrons between the polar or directionally charged molecules. Materials which are covalently bonded are good insulators and are found in polymers, water molecules, and in diamond crystals. Metallic bonds are good conductors both thermally and electrically because their electrons are held in an "electron cloud" which permits more mobility of the electrons. Dental amalgam and all casting alloys are bonded by metallic bonds.

Secondary bonds (van der Waals forces, and chelation) are weak bonds formed through the polarization of molecules. Covalently bonded materials, such as denture impression compound which becomes plastic after heating, exhibit thermoplastic change. This change in state occurs through the relaxation of van der Waals forces and not because of the cleavage of covalent bonds within the polymer chain of the resin component of the impression compound (2). Chelation which occurs through ion substitution, is reported to be present in the adhesion mechanism of polycarboxylate cement to tooth enamel. The chelation of polycarboxylate cement to enamel occurs through the periodic bonding of the polymer matrix of polyacrylic acid to calcium ions of enamel.

#### Optical Properties

The esthetic qualities of restorative dental materials can be one of the most perplexing considerations in modern dentistry. Optical properties result from the visual perception of a very narrow band of electromagnetic radiation (the visible spectrum = 400 to 700 nm) (3,4). When an incident beam of light strikes an object only two reactions can occur, the light beam will either be scattered or absorbed. When a reflected (scattered) beam of light is observed, it is subconsciously determined to be a color because we perceive it within the visible spectrum (5,6).

Colors can be measured by two systems--visually by the Munsell Color Order System and instrumentally by the standards of the Commission Internationale de l'Eclairage (commonly called the C.I.E.). The Munsell Color Order System consists of three color parameters. Value, the relative amount of lightness or darkness in a color, can be altered by pigments; chroma (or saturation), the intensity of a color, can be increased by staining procedures; and hue, the name of a color, is difficult to modify (7).

The instrumental measurement of color determines the percentage of reflectance of light at each wavelength and this measurement is compared to a color standard at each wavelength. Through mathematical calculations, a plot of the color can be produced on a chromaticity diagram. The coordinates of this plot are used to determine the parameters of color, as described by Grassman, which are luminous reflectance, dominant wavelength, and excitation purity. Each of the Grassman parameters can be transposed into the Munsell Color System (luminous reflectance = value, excitation purity = chroma, and dominant wavelength = hue) (8).

Colors can be mixed in a complex yet orderly fashion to yield predictable results. In dentistry, we use the subtractive mixing of pigments to yield desired colors. In the subtractive color system, the primary colors are red, blue, and green. When two primary colors are mixed a secondary color is produced. In the subtractive color system, the secondary colors (yellow, magenta, and cyan or violet) are the primary colors of the additive color system. Similarly, the primary colors of the additive color system are the secondary colors of the subtractive color system. White results from mixing all of primary colors of the subtractive color system, and black results from the mixing of all primary colors of the additive color system. Metamerism is a visual phenomenon which occurs when two objects appear to be the same color in a light source of one wavelength and appear to be different colors in a second light source of wavelength different from the first (9).

#### Electrochemical Properties

Electrochemical properties can be determined from a table of oxidation-reduction potentials. This table describes how easily an ion will react. The susceptibility of materials to tarnish and corrode is based upon this property. Gold, which is poorly reactive and the least likely metal to tarnish, is highly electropositive (+1.498 volts). Potassium, which is a highly reactive metal and will react with explosive force, is electronegative (-2.925 volts). In dentistry, sulfide and chloride ions present the greatest tarnish and corrosion problems to metals (10).

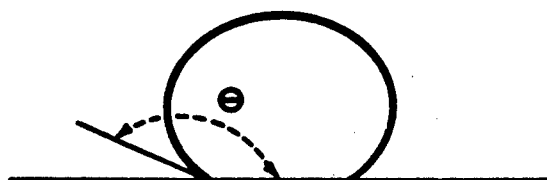
#### Surface Phenomena

Surface properties are used to describe the wetting of a substrate surface by a liquid. Surface properties are a function of the surface tension of the liquid (oil has a high value of surface tension and does not spread easily over a surface) and the surface free energy of the solid (teflon and silicone have low values of surface free energy and resist wetting of their surfaces). The spread of a drop of liquid on a substrate surface is an indication of the wetting of that surface by the liquid. By measuring the contact angle between a liquid and a substrate surface, the degree of wetting can be measured directly (Fig 1). If the liquid does not wet the substrate well, then the interfacial contact angle will be large (approaching 90 degrees); and the substrate is called "hydrophobic." If the same liquid wets a different substrate surface well, the interfacial contact angle between a second substrate

surface and the liquid will be small; and the second substrate is called "hydrophilic" (11).

The protein-rich saliva layer covering human teeth, called "biolayer" (12) (or pellicle), should be removed to achieve the best adhesion between prepared tooth and cast restoration. The biolayer can be removed with cement liquid or a surfactant before cementing a cast restoration to tooth structure.

Capillary penetration is microleakage of a fluid into a confined space (as between a restoration and the cavity wall). Capillary penetration is dependent upon the size of the interfacial space, the surface tension of the fluid, and the surface free energies of the interfacial materials (usually tooth structure and a restorative material) (13).



**A - HIGH CONTACT ANGLE**  
**"POOR WETTING"**



**B - LOW CONTACT ANGLE**  
**"GOOD WETTING"**

*Figure 1. Wetting of a liquid on a solid. A. High contact angle is an indication of poor wetting. B. Low contact angle is an indication of good wetting.*



### Thermal Expansion

The coefficient of thermal expansion is used to predict the expansion or contraction of materials and is quantified in a ratio of expansion or contraction per degree Centigrade. Drastic mismatches in the coefficients of thermal expansion between tooth structure and restorative material can result in an increased potential for microleakage at the interface of the restorative material and tooth structure. Similarly, if a porcelain and a ceramo-metal are extremely mismatched, catastrophic bond failure between the porcelain and the ceramo-metal will result (14).

## MECHANICAL PROPERTIES\*

### Strength

Compressive strength is a measure of the force necessary to fracture a material by two opposing forces directed toward each other within the same plane. The compressive strength of most brittle materials is greater than any of the other strength values, and is determined by fracturing small cylinders of the material.

Tensile strength is a measure of the force necessary to rupture a material by two opposing forces directed away from each other. Most brittle materials are weakest in tensile strength. To conserve material, tensile testing of brittle materials is usually conducted using the "diametrial tensile test" (Brazilian Test) (Fig 2). In the diametrial tensile test, a compressive force is applied to a circular specimen, fracturing the specimen through its diameter because of internal tensile strain. From this test, the tensile strength and modulus of elasticity can be calculated.

Shear strength is a measure of the force necessary to rupture a material by two opposing parallel forces directed toward each other but not in the same plane. For most materials, shear strength values are intermediate between compressive strength and tensile strength values.

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\* Volumes by Craig (15), O'Brien and Ryge (16), and Phillips (17) are excellent references and the basic information varies little from one text to another.

Torsion (twisting) and bending (flexing) are compound forces which are better described by other strength properties (bending is a combination of compression and tension).

#### Stress and Strain

Stress is the force per unit area applied to a material. Stress concentrations, such as cracks and surface flaws, can focus the stress into specific areas. The stress is increased through concentration and, consequently, the stress concentrations create forces great enough to cause catastrophic failure.

Strain is the internal dimensional manifestation of an externally applied force or stress. Strain is also described as the change in length compared to the original length ( $L/L_0$ ). Most materials change dimension upon setting which will create strain within the material. There are four types of strain--elastic strain, plastic strain, creep or viscous flow, and viscoelastic strain.

Elastic strain is the temporary distortion of a material by an applied stress. When the stress is removed, the material will return to its original shape or form. An example of elastic strain is the stretching of a rubber band.

Plastic strain is the permanent distortion of a material. Modification of its shape or form is usually evident after the applied stress is removed. An example of plastic strain is a deformed wire paper clip.

Viscosity is the resistance of a fluid to flow. If the viscosity of a fluid increases at the same rate as the applied force, it is called newtonian; if the viscosity increases at a greater rate than the applied force, it is termed dilatant; but, if the viscosity of a fluid decreases as the force upon it increases, it is called pseudoplastic. Water is a newtonian fluid, rubber base impression material expressed from a syringe (or polycarboxylate cement expressed from the inside of a cast restoration) is pseudoplastic, and fluid denture resin is considered to be a dilatant fluid.

Creep or viscous flow is elastic strain and plastic strain within the same system. Creep is a function of time and applied stress. Certain complex metals, like dental amalgam, exhibit creep when placed under an applied stress. The creep in dental amalgam occurs by the slippage of the weaker phases like the gamma II phase.

Viscoelasticity, which occurs in dental impression materials (elastomeric materials), is a variation of creep. Viscoelasticity has two components, the viscous nonrecoverable flow and the elastic recoverable component. Viscoelasticity can be illustrated by improperly inverting a rubber base impression on a hard surface for a prolonged period. When the impression is examined, the indentation of the surface can be seen in the impression. The indentation in the surface of the impression is the result of viscous and elastic flow of the impression in contact with the hard surface. With time, the size of the surface indentation will decrease slightly as the elastic component recovers. Because of the property of viscoelasticity, elastomeric impression materials must be allowed to recover from the elastic deformation caused by removal of the impression from intraoral undercuts before dental stone is poured into an impression.

#### Modulus of Elasticity

Modulus of elasticity or Hooke's Law is a measure of the relative stiffness, rigidity, or resistance to deformation of a material. This property can be determined by a ratio of the applied stress to the resulting strain (Fig 3). Hooke's Law states that for a given material, stress is directly proportional to strain within the elastic range (the recoverable range).

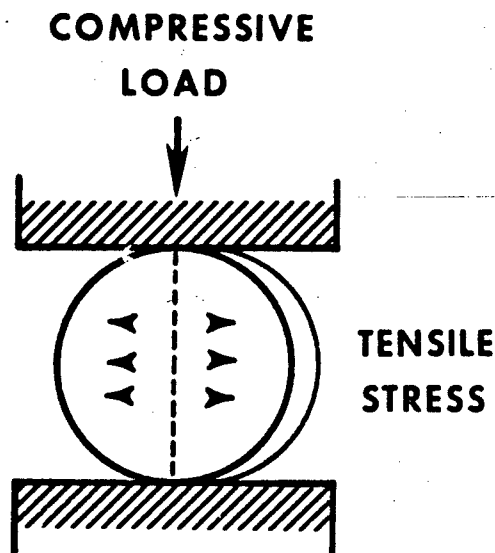


Figure 2. Diametral tensile test. Compressive force produces tensile stress (arrows).

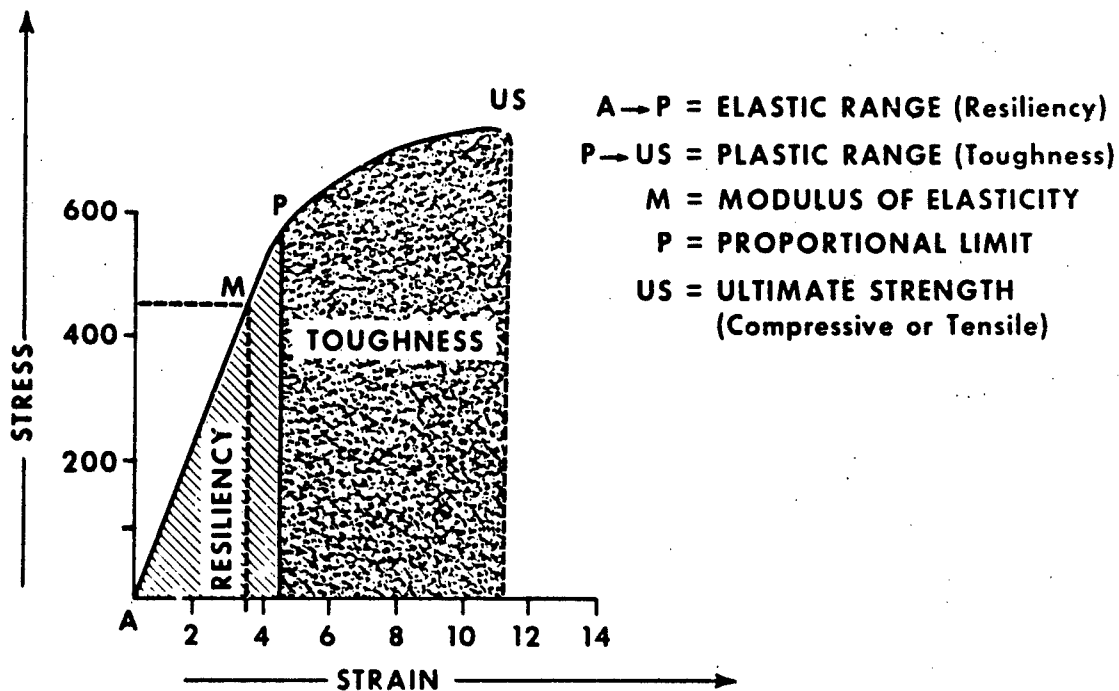


Figure 3. Illustration of the ratio of applied stress to resulting strain.

The modulus of elasticity of a given material is a constant. Cold-working (strain-working) or heat-treating a material will not alter the modulus of elasticity. Cold-working and heat-treating may alter other mechanical properties like proportional limit, yield strength, and ultimate tensile strength. Modulus of elasticity may be determined by either compression or tensile loading. Higher modulus indicates greater rigidity but does not indicate higher strength; for example, a rubber band has a very low value of modulus of elasticity (low rigidity) but requires a great force to break it in tensile load (indicating high strength).

Yield strength is a measure of the stress needed to deform a material permanently. There is a degree of measurement variability in the determination of yield strength. The selection of the "per cent offset" is determined by the researcher and can be preset to a high or low value which will yield biased values of yield strength. The per cent offset is the position on the horizontal axis of a stress-strain diagram from which the yield strength measurement is started. For most dental research, a 0.1% or 0.2% offset is considered standard. Yield strength is

determined by a line drawn parallel to the stress-strain curve. The point of intersection of the yield strength line with the stress-strain curve is the yield strength of the material (in units of force/area) at that per cent offset (Fig 4).

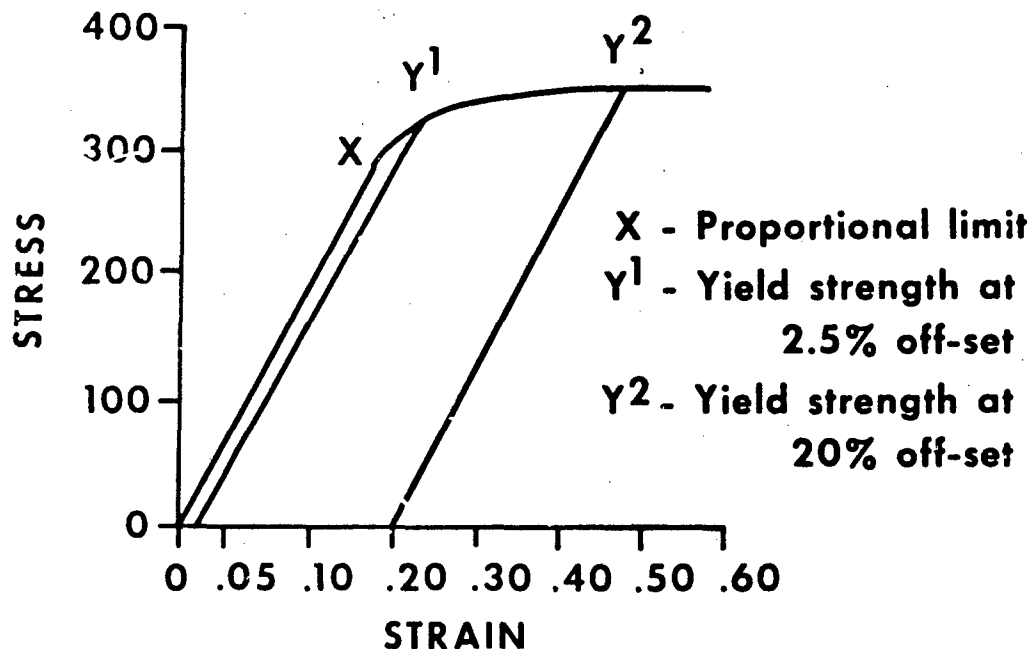


Figure 4. Per cent off-set yield strength at 2.5% (y<sup>1</sup>) and 20% (y<sup>2</sup>).

Hardness is a measure of the resistance of a material to indentation and is often improperly related to wear. Wear is best measured by simulated clinical testing using a machine designed to force a material against a rotating or oscillating flat, abrasive surface. Different indentation instruments are used to measure hardness of different materials. Higher hardness numbers indicate harder materials. Soft plastics and rubbers are measured with a Shore A Durometer, and harder plastics and soft metals are measured with either a Rockwell or Brinell indenter. The Knoop microindenter is a diamond tipped and diamond-shaped instrument used to determine the hardness of very hard materials like porcelain, tooth enamel, and hard metals. The Vickers microindenter is a square-shaped diamond-tipped instrument, and is similar to the Knoop microindenter. The Vickers microindenter, which is mainly used in Europe, is required in reporting ADA specification test results on dental casting alloys (18).

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## NOTES





## CHAPTER II

## DENTAL AMALGAM

Dental amalgam was first used by the Chinese as a restorative material in the seventh century A.D. Abuse of this material stimulated organized dentists in the nineteenth century to ban dental amalgam for human use (1). Through judicious experimentation, the properties of dental amalgam have been improved, and today dental amalgam is the most commonly used dental restorative material (2).

This chapter contains a discussion of the classification of conventional and high-copper amalgam, the handling characteristics, and the function of the component metals. It will conclude with a brief comment on mercury toxicity.

## CLASSIFICATION OF DENTAL AMALGAMS

## Conventional (Table 1)

G. V. Black characterized the detrimental properties of dental amalgam. His research, which is considered the most significant in the early development of dental amalgam, eventually lead to improved setting expansion and strength of dental amalgam (3). Black's original dental amalgam alloy formula was 73.2% silver and 26.8% tin. He is credited with the discovery of the beneficial effects of annealing amalgam alloy. Heating an alloy decreases the amount of beta phase (Table 2) and relieves internal stresses within the alloy which can alter the setting time (4).

Alloy-mercury ratios of 1:4 were commonly used several decades ago because a high mercury content was necessary to properly wet the poorly refined alloys. The older alloys had a wide variation in particle size, and the larger particles were seldom wet adequately. The procedure required squeezing the mixed amalgam in a linen cloth to remove the excess mercury. Eames introduced the "Eames

technique (5)\* to decrease the mercury content in the mixed amalgam without squeezing the mixture. His technique required a 1:1 ratio of alloy to mercury and necessitated careful proportioning of the amalgam. Today amalgam alloys are refined to a purer quality and there is a narrower range of particle sizes; hence, neither squeezing nor the Eames technique is necessary to wet the alloy with the mercury adequately. Currently, alloy-mercury ratios in conventional amalgams are about 2:3.

Early amalgam alloys were supplied only in lathe-cut particles. The particles were prepared by filing cast ingots of silver-tin. Refinements in the preparation of the particles resulted in alloys with more uniform particle sizes and better handling properties. Spherical particles were introduced in the late 1960s. Amalgams with spherical particles require different manipulation than amalgams with lathe-cut particles (less packing pressure with a larger plugger and more lateral condensation).

Gayler (6) identified the  $\gamma_2$  phase in conventional dental amalgam using phase diagrams. (The phases of conventional and high-copper amalgams are listed in Table 2). Ryge et al (7), in a study of amalgam using X-ray diffraction, disputed the presence of the  $\beta_1$  phase.

#### High Copper (Table 1)

High copper amalgams have developed through the research on conventional amalgam and variations in its formulation. Wagner (8) in 1962 (working for Degussa in Europe) identified  $\gamma_2$  as the most corrosive phase in conventional amalgam. Wagner found that corrosion propagated from the occlusal surface to the pulpal floor. Jorgensen (9) hypothesized that the  $\gamma_2$  phase was responsible for marginal breakdown because of high corrosion of the  $\gamma_2$  phase and subsequent voids formed by the further breakdown of the  $\gamma_2$  phase (this is widely disputed). Jorgensen (9) proposed a silver-palladium alloy, but it had an unacceptable setting expansion and setting time. Mateer and Reitz (10) analyzed the corrosion products (Table 3) of dental amalgam and found that tin was the principal metallic ion involved in amalgam corrosion.

Johnson (11) suggested an amalgam formulation of 64% Ag + 26% Sn + 10% Au. In this formulation, the gold combined with the tin to eliminate the  $\gamma_2$  phase. Although the model formulation worked well, the prohibitive price of gold prevented commercial production of this alloy.

Youdelis and Innes (12) proposed a copper-containing amalgam which they reported strengthened the set amalgam by a "dispersed phase" of silver-copper eutectic alloy (a eutectic alloy is a binary alloy of specific proportion which has a lower melting point than either of the two parent metals). The strengthening mechanism is based upon the theory that dispersed particles of silver-copper eutectic would retard the propagation of cracks within the amalgam by blocking the cracks and strengthening the set amalgam. The silver-copper eutectic does not strengthen the set amalgam by "dispersion hardening" but through the reduction of the  $\gamma_2$  phase. The copper draws tin ions from the  $\gamma_2$  phase to form  $Cu_6-Sn_5$ , which frees silver to combine with mercury to form  $Ag_3-Hg_2$ . The reaction time of the copper with tin is controversial; the slow reaction may be initiated when the amalgam reaches mouth temperature and may progress for up to 24 hours; the reaction of copper-silver may not occur at all, which indicates that there is no  $\gamma_2$  phase formed in high-copper amalgams.

Admix amalgam alloy is a blend of lathe-cut and spherical particles. The first commercial admix alloy was Dispersalloy (Johnson and Johnson); it was based upon the work of Youdelis and Innes (12). This amalgam alloy is fabricated in two steps; first, the silver-tin is lathe-cut from ingots of silver-tin alloy, which is the same process used to produce conventional  $\gamma_2$  containing amalgam alloy; second, spherical particles of silver-copper eutectic are produced by spraying the molten alloy through a fine orifice into a liquid. Hence, the resulting alloy is a blend of lathe-cut and spherical particles is called an "admix amalgam alloy".

Unicompositional amalgam alloys are alloys composed only of spherical particles. Asgar and Reichman (14) are credited with the development of the first high copper unicompositional alloy. The spherical particles are formed by forcing molten alloy of silver-copper-tin through an orifice into a liquid. The resulting spherical particles have a core of tin with silver on the periphery, and copper found throughout the sphere. The first amalgam product produced by this process was Tytin (S.S. White Inc.). The term which describes this general group of amalgam alloys is "unicompositional amalgam alloys". Tytin has a fast setting time because of the diminished beta phase and because of the small particle size of the Tytin alloy.

Tytin has been linked to numerous reports of postoperative pain. In a recent clinical study, Mahler and

Nelson (15) found that Tytin had a statistically greater amount of marginal leakage than an admix amalgam alloy (Dispersalloy) handled in the same manner. These investigators were unable to explain the increased marginal leakage of Tytin because the setting shrinkage, creep, and other physical properties of both amalgams are the same.

#### HANDLING CHARACTERISTICS

Cavity varnish can be used on dentin surfaces before the insertion of high copper or conventional amalgams to diminish the problem of tooth sensitivity from microleakage of oral fluids into the interface between tooth structure and restorative material. Conventional amalgam is still advocated by some practitioners because of its high corrosion and setting expansion which they feel seals the interface between tooth structure and amalgam.

Amalgams which set quickly, can be finished at the same appointment in which the amalgam is placed. Dahi et al (16) have described a technique called the "eight-minute-polish". This study by Dahi et al (16), evolved from a 3 year clinical evaluation of Tytin amalgam alloy polished 24 hours after placement and 8 minutes after trituration. Using scanning electron microscopy, they found no significant difference between the two polishing techniques. The "eight-minute-polish" procedure consists of using a rubber cup and a slurry of triple fine Silux powder.

#### MERCURY TOXICITY

The potential hazards of mercury toxicity should be recognized by the dentist and explained to the staff and patients. After a review of the literature on mercury toxicity and mercury sensitivity from dental amalgam, Bauer and First (17) stated that, "for the dental assistant and dentist, the amount of mercury exposure during an average day with good mercury hygiene is not toxic" and "for the dental patient the concern of risk or potential hazard from mercurial poisoning is virtually non-existent." Bauer and First (17) also explain that mercury sensitivity is a rare self-limiting reaction. The dentist should be aware of the symptoms of allergic reaction, and should handle each situation as the severity and duration of the allergic reaction dictate.

## COMMENT

The proper use of modern dental amalgam can be easily accomplished despite its complex content and reactivity. It is imperative that the clinician have a complete understanding of all the manipulative variables (Table 4) involved in the use of dental amalgam and how to most advantageously control their properties.

TABLE 1  
CLASSIFICATION of DENTAL AMALGAMS

Copper Content	Morphology	Products and Manufacturers
Conventional amalgam	lathe-cut alloy	Aristalloy (Baker) Optalloy (Caulk)
	spherical alloy	Spheralloy (Kerr) Accusphere (Litton) Spherical (S.S.White)
High-copper amalgam	admix alloy *	Dispersalloy (J&J) Optalloy II (Caulk) Micro II (Caulk) Ease (Caulk) Cupralloy (Star) Phasealloy (Phasealloy Co.)
	unicompositional alloy	Tytin (S.S.White) Sybralloy (Kerr) Indiloy (Shofu) Valiant (Caulk)

\* Admix amalgam alloys are often called "dispersed phase alloys"; this is an improper term. The strengthening mechanism is reduction of the  $\gamma_2$  phase and not dispersion hardening.

TABLE 2

## COMPOSITION OF COMMON PHASES IN DENTAL AMALGAMS

Type of Amalgam	Phase	Composition
Conventional amalgam	beta	Ag-Sn
	beta <sub>1</sub>	Ag-Hg
	gamma	Ag <sub>3</sub> -Sn
	gamma <sub>1</sub>	Ag <sub>2</sub> -Hg <sub>3</sub>
	gamma <sub>2</sub>	Sn <sub>7</sub> -8Hg
High-copper amalgam	High copper amalgam initially contains the same phases as conventional amalgam plus, after the reaction of copper, the following additional phases.	
	nu	Cu <sub>6</sub> -Sn <sub>5</sub>
	epsilon	Cu <sub>3</sub> -Sn

TABLE 3  
FUNCTION OF METALS IN DENTAL AMALGAM

Metal	Increases	Decreases	Corrosion Products
Silver	strength expansion reactivity	creep	silver-chloride silver-sulfide
Copper	strength expansion hardness	creep	copper-oxide copper-sulfide
Tin	reactivity corrosion	strength hardness	tin-oxide tin-chloride tin-sulfide
Indium	(used interchangeably with tin in Indaloy)		
Zinc	plasticity strength Hg/alloy-ratio	creep shrinkage *	zinc-chloride zinc-oxide
Palladium	strength	corrosion **	none

\* Zinc setting in the presence of water, increases the expansion of conventional amalgam, Johnson and Paffenbarger (13) found that zinc decreased the shrinkage in the absence of water.

\*\* Only 1/2-1% palladium is necessary to make amalgam tarnish and corrosion resistant.

TABLE 4  
HANDLING PROPERTIES OF DENTAL AMALGAM

Manipulation	Conventional	High-Copper
Over-trituration	increased strength increased creep decreased expansion	decreased strength increased creep
Under-trituration	will not mix	decreased strength
Excess-mercury	gamma <sub>2</sub> formation	gamma <sub>2</sub> formation
Condensation-pressure	sphericals require less	sphericals require less
Prolonged-condensation	little effect	Fast-setting amalgams will be weakened
Cavity sealer	not essential	Essential *

\* Most high copper and conventional amalgams shrink upon setting, Dispersalloy's shrinkage is almost zero (18).



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## CHAPTER III

## RESIN RESTORATIVE MATERIALS

Introduced in 1937, resin restorations (resin without a filler) were dependent upon heat to activate the chemical polymerization of the polymethylmethacrylate component. It was not until 1947 that a means of chemically activating these resin restorative materials was developed (hence the term "cold cure"). In 1950, R.L. Bowen introduced a resin restorative material consisting of quartz filler coated with a binder of vinyl silane in a polymer matrix derived from bisphenol and glycidyl acrylate (1). In the last fifteen years, composite restorative materials have been introduced with matrices derived from many different monomers and filled with materials of varying particle size and wear resistance. The introduction of ultraviolet activating systems in 1965 led to the development of visible light-activated composite resin restorative materials currently in use. The vast list of possible choices of resin restorative material necessitates a clear understanding of the different systems available, their uses, and properties (Table 1).

This chapter is organized into five sections--resin restorative materials (unfilled, fully filled, and microfilled resins), tooth preparation and modifications, activation systems, finishing and polishing, and new developments in dental resin restorative materials. The chapter contains some historic and descriptive information, some advantages and disadvantages of the different materials and activation systems, and some warnings about contraindications for the use of posterior composite resins and cermet systems.

## RESIN RESTORATIVE MATERIALS

## Unfilled

Restorative materials made of unfilled resin are classified by ADA Specification 27 as a Type I direct

filling resin. Unfilled resin materials are generally composed of liquid monomer and powder polymer mixed in a ratio of 1 part liquid to 3 parts powder. The bonding and glazing agents of most composite resin restorative materials are usually unfilled monomer which is the same as or is compatible with the monomer of the filled system. Glazing and bonding agents are mixed in a 1:1 ratio. These materials are usually chemically activated by mixing the two unfilled components of the system. Unfilled resin restorative materials are used primarily as repair materials for porcelain-metal restorations, bonding agents for filled composite resin materials, and bonding agents for acid etched fixed partial dentures. The use of unfilled resins as direct filling materials and glazing agents has been discarded.

TABLE 1

## PROPERTIES OF RESIN RESTORATIVE MATERIALS

Property	Unfilled Resin	Conventional Composite	Microfilled Composite
Tensile strength (MPa)	24	45	32
Modulus of elasticity (MPa.)	0.24	13.7	4.5
Polymerization shrinkage	7%	1.4%	1.7%
Thermal expansion ( $\times 10^{-6}/^{\circ}\text{C.}$ )	92	35	59.9
Water sorption mg./cm <sup>2</sup> (14 days) (color change)	1.7	0.6	1.4
Wear resistance	lowest	highest	intermediate

Note: These are average values and are intended to yield comparative information only.

### Fully Filled or Conventional Composite

Conventional composite resin restorative materials are classified by ADA Specification 27 as Type II direct filling resins (2). Conventional composite resin restorative materials have a monomer component similar to bisphenol and glycidyl acrylate (3) and filler material like quartz or glass with particle sizes from 5 to 30 microns. The filler to polymer matrix ratio is 1 to 1. These materials are activated chemically by mixing two components of the system or by using a light source.

### Microfilled Composite

Microfilled composite resin restorative materials are classified by ADA Specification 27 as Type I direct filling resins. Microfilled composites contain vinyl silane coated colloidal silica particles (also called aerosil) which have a diameter of less than 0.05 microns. The filler to matrix ratio is seldom more than 1 to 2. Degussa Inc. (Frankfurt, Germany) is the sole distributor of this filler material. The use of different filler results in properties for microfilled composites which differ from conventional composites.

Both conventional and microfilled composite restorative materials primarily are used as direct filling restorative materials in Class I, III, and IV cavity preparations and in repair of porcelain-metal restorations (Table 2).

## TOOTH PREPARATION AND MODIFICATIONS

Etching is mandatory for microfilled composite resin restorative materials. The etchant is generally a phosphoric acid (35% concentration). It is important to keep the tooth wet during the etching procedure; if the etched enamel surface is allowed to dry, calcium phosphate salts will form on the surface and inhibit the resin bonding agent from adhering to the surface of the enamel. The 3-M product "Scotchbond" appears to enhance adhesion of microfilled and conventional composites; but little research data are available on this material.

Controversy exists on the type of cavo-surface margin to be used in Class II preparations. Most clinicians feel that a butt joint is best in stress-bearing areas. It should be emphasized that a white line can be seen at the margins of most microfilled composite restorations if no bevel is placed.

TABLE 2  
EXAMPLES OF RESIN RESTORATIVE MATERIALS  
PARTICLE SIZES AND MANUFACTURERS

Brand Name and Mfg.	Filler	Activation
Bondfil (L.D.Caulk)	unfilled	chemical
Servitron (Ash/Densply)	unfilled	chemical
bonding agents of most systems	unfilled or slightly filled	chemical
Adaptic (Johnson & Johnson)	quartz (10-30) microns	chemical
Concise (3-M)	quartz (10) microns	chemical
Silar (3-M)	aerosil (0.04 microns)	chemical
Finesr (L.D.Caulk)	aerosil (0.04 microns)	chemical
Command (Kerr)	lithium aluminum silicate "ultrafine" = (1 micron)	visible light
Prisma (L.D.Caulk)	barium glass (1-5 microns)	visible light
Visar-Fil (Dent Mat)	barium glass + silicon dioxide (3.0 microns)	visible light
Ultra Bond (Dent Mat)	barium glass (3.5 microns)	visible light
Getz (Teledyne)	quartz (8-10 microns)	visible light
Superfil (Bosworth)	unknown (0.3 microns) (as reported by Mfg.)	visible light
Lite (Phasealloy)	aerosil (0.04 microns)	visible light
Sillux (3-M)	aerosil (0.04 microns)	visible light

Zinc oxide and eugenol materials and resin cavity varnishes are contraindicated for use with all resin restorative materials. S.S. White has a varnish of methyl cellulose which does not appear to affect the organic matrix in resin restorations. Low strength disalicylate bases, like "Dycal" (L.D.Caulk) and "Life" (Kerr), can be used to cover dentin surfaces in place of zinc oxide and eugenol materials (eugenol inhibits the set of the organic matrix material).

#### ACTIVATION SYSTEMS

##### Chemical

Chemically activated resin restorative materials contain a cross-linked resin with a peroxide initiator and an amine accelerator. Using 20% more or less of one component of this system will not affect the setting time.

##### Ultraviolet Light (UV)

With ultraviolet light activation systems, patients are subjected to a definite health risk from overexposure to unshielded UV radiation. The UV lamps do not maintain a constant magnitude of radiant energy (the lamps loose their focus). It is difficult to determine when the UV component has been exhausted because UV light is out of the visible range (400 to 700 nm). The depth of cure for UV systems is about 1/2 to 1/5 that of the visible light activated-systems.

##### Visible Light

Visible light-activated systems contain camphor quinone and an amine to absorb the light. The unpolymerized visible light-activated composite resin must be protected from any light source and are therefore packaged in black tubes. The depth of cure for light-activated systems is about 5 mm, with the surface closest to the light source being the hardest. Darker shades have more resistance to polymerization and result in shallower depths of cure(4). Polymerization may continue for up to five minutes after the lamp is turned off, hence finishing and polishing is best done 10 minutes after the visible light-activation has ended. The light source for the visible light-activated system is a small projector light bulb with a blue filter, producing a light of about 400 nm. When used in a syringe,

the visible light-activated composite system can yield bubble free restorations with adequate working time by using a safe dependable activation light source.

#### FINISHING AND POLISHING

Mylar strip provides the smoothest surface for resin restorative materials. Silicon carbide extra-extra-fine and tin oxide can be used to provide a smooth surface on composites. Diamonds should be avoided on microfilled composites because they tend to melt the resin matrix and clog the diamond stone. Microfilled composites are easier to finish (less wear resistance) than conventional composites, but consideration must be given to the greater color stability of conventional composites.

#### NEW DEVELOPMENTS

Use of composite resin restorative materials in posterior teeth (Class I and II) should be given serious thought (5). The most recent clinical research has shown these materials to be a poor second to silver amalgam restorations, with less than 50% survival rate for composite after 5 years.

Composite resin materials are currently being developed which are hydrophobic (they inhibit the imbibition of water or water soluble pigments into their mass). These materials should be more color stable than composites currently available (6).

The Espe Co. is developing a new material called "Cermet" which is ceramic and metal combined with polyacrylic acid for use in Class II and III cavity preparations. To date, this material appears to have good wear resistance but is an unesthetic gray.



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## NOTES

## CHAPTER IV

## DENTAL CEMENTS, BASES, AND LINERS

Dental cements are used in permanent cementation, temporary cementation, bases, and cavity liners (1,2). According to ADA Specification 8, Type I zinc cement must have a film thickness of 25 microns or less, and Type II zinc cement must have a film thickness of no more than 40 microns. Permanent cements generally have higher strength properties and are less soluble than temporary cements. The single most important strength property of dental cements is tensile strength. Farah et al (3) demonstrated that, even when cement is used as a base material under dental amalgam, significant tensile forces are placed upon the cement. All dental cements are weaker in tension than compression. Solubility of dental cements is not only a function of the kind of dental cement but also how the cement is mixed and placed. In cementation, dental cements are intended to seal the margins of restorations. This function assumes the castings being cemented are the proper fit in all marginal areas. There is no relation between the retention of a casting before and after cementation (4). Vented cast restorations can be seated further than unvented castings (5).

This chapter contains information about permanent and temporary cement as well as base materials and cavity liners (Table 1). It includes descriptions of uses of cement bases and liners (Table 2), and a list of products and manufacturers to help the clinician determine the most appropriate material for each situation.

## PERMANENT DENTAL CEMENTS

## Zinc Phosphate

Zinc phosphate cement has been in use in dentistry for almost 100 years and still stands as the standard against which other cements are measured. The powder of this cement is composed of zinc oxide with about 10% magnesium

oxide; the liquid is orthophosphoric acid buffered with small amounts of aluminum phosphate and calcium phosphate. Because of the high acidity of the set cement, zinc phosphate cements composed of red and black copper should not be used on vital teeth. The reaction rate of a zinc phosphate cement mixture can be affected by a number of factors (Table 3) (6).

When zinc phosphate cement is allowed to set in contact with water, "hopite crystals" of zinc phosphate will form which are more soluble than amorphous zinc phosphate which forms normally in a dry environment. The use of cold slab and frozen slab techniques have proven to be beneficial in the cementation of large numbers of restorations or orthodontic bands. When a cold mixing slab (7 to 21° C) is used, more powder will be incorporated into the liquid and the set of the cement mixture can be prolonged (up to 3 times) until the mixture is warmed (mouth temperature); then, the setting reaction will proceed rapidly.

If a frozen mixing slab is used (-10 to 6° C), there will be more water in the mixture from water condensation on the slab, but compensation can be made for condensation by incorporating more powder into the mixture. The final mixture will still have a prolonged setting time (up to 9 minutes), and setting will be activated by increased temperature (mouth temperature).

If the powder is incorporated into the liquid mixture slowly (mixing time should be around 90 sec), the aluminum and calcium ions have a greater neutralization effect on the phosphoric acid than if the powder is incorporated in less than 90 seconds. This phenomenon is called "slaking."

#### Silicophosphate

Silicophosphate cements have a powder component which contain about 20% zinc oxide and 40% silica ( $\text{SiO}_2$ ) which imparts the translucent property to the cement. The powder also contains calcium and sodium fluoride which leach out of the set cement when it contacts water, acids, or saliva. The fluoride may provide some anticariogenic properties to the tooth structure. The addition of metallic oxide pigments to the powder provides a narrow range of shades which can be used with translucent porcelain jacket crowns to improve the optical properties of the porcelain.

The liquid component of silicophosphate cement is about 40% phosphoric acid buffered with aluminum phosphate and

zinc phosphate. The liquid readily absorbs or loses water if not sealed well after each use, and the alteration in water content can affect the properties of the cement.

Silicophosphate cement can be mixed completely within one minute because little exothermic heat is released by the setting reaction. The acidity of the cement is quite high and can cause adverse reactions if placed too close to vital pulpal tissues.

The tensile and compressive strength values for silicophosphate cement are greater than zinc phosphate cement, but silicophosphate cement is more soluble than zinc phosphate cement. All of the factors which affect zinc phosphate cement also affect silicophosphate cement, except for liberation of the heat of reaction. Particle size of silicophosphate cement is about 40 microns, and hence, it is classified by Specification 8 as a Type II cement.

#### Zinc polycarboxylate

This cement was developed about fifteen years ago by Dennis Smith. Controversy surrounds the adhesive properties of polycarboxylate cement which are thought to be based upon a chemical reaction between the carboxylate polymer of the cement liquid and the calcium ions of the tooth structure (called a "chelation reaction"). To date, no definitive studies have demonstrated the reaction to vital tooth structure. As the powder (which in most cases is similar to the powder in zinc phosphate cement) is mixed with the liquid (which is normally a viscous polymer of polyacrylic acid), a polymerization reaction occurs between the polyacrylic acid liquid and the zinc ions of the powder. If the cement is placed in contact with a heavy concentration of calcium ions, as in enamel, chelation can occur between the setting polymer matrix and the calcium ions in the tooth structure. The reaction rate is only slightly greater between the polyacrylic acid and the zinc ions in the powder component. If the mixed cement is placed in contact with tooth structure too long after the initiation of mixing, little chelation between the calcium in the tooth structure and the polymer can occur. Fluoride has been added to the powder to enhance the strength and manipulative properties of polycarboxylate cement, but the fluoride does not leach out of the set cement as it does in silicophosphate cement.

Dennison and Powers (2) found the strength values of this cement to be close to those of zinc phosphate cement. Strength values for polycarboxylate cement are difficult to

achieve because polycarboxylate is an amorphous polymer matrix and has the property of flow-with-time-and-pressure (creep).

The literature is replete with studies presenting conflicting strength values for polycarboxylate cement. Also, studies are not consistent in comparing its solubility. Some studies of its solubility in distilled water show polycarboxylate cement less soluble than zinc phosphate cement, and other studies of its solubility in acid and bases show a greater solubility for polycarboxylate cement than for zinc phosphate cement. Contamination of the cement with saliva can result in catastrophic bond failure weeks or months after cementation. The presence of a protein layer on the tooth structure (bio-layer or pellicle) will inhibit chelation with tooth structure. The strength of this cement can be increased by addition of more powder to the liquid, but this diminishes the potential for chelation with tooth structure (7).

NOTE: There is strong concern today that the chelation of polycarboxylate cement with tooth structure may not be a reality but may be a manifestation of the reaction of the cement polymer with inorganic surface ions not commonly occurring in tooth structure (as fluoride).

#### TEMPORARY CEMENTS

##### Zinc Oxide and Eugenol

Zinc oxide and eugenol cements comprise a large group of dental cements and are used as cements and bases. The basic components are zinc oxide in powder or paste form and eugenol or clove oil liquid. Zinc acetate or acetic acid in the liquid component is necessary for the acceleration of the cement set, but water can also act as an accelerator for the set reaction. The medicinal properties of eugenol cannot be underrated; the bacteriocidal effects of eugenol can last for many weeks after placement in the mouth. The high solubility of zinc oxide eugenol cements potentate the prolonged bacteriocidal effects of the eugenol component. The obtunding qualities of eugenol (or clove oil) have been appreciated for centuries, but controversy exists over the mechanism of action of eugenol upon the dental pulp. Brannstrom and Nyborg (8) have demonstrated that eugenol may have little direct beneficial effect upon the dental

pulp, but may actually kill bacteria in the dentinal tubules and eliminate the source of pulpal irritation which renders the pulpal reparative mechanism more capable of function.

Additives have been used to increase the poor strength properties of zinc oxide eugenol cements, but the solubility of these modified cements is high, which eliminates them from routine use with cast restorations. Additives may be polymer beads or fibers in the powder as IRM, B&T or Fynal (by L.D. Caulk); or, ethoxybenzoic acid may be added to the liquid as in EBA cements.

#### Acrylic Resin

The principal component of this cement is methyl methacrylate. These cements are available for cementation of cast restorations; but film thickness of the acrylic cements is beyond acceptable limits (about 90 microns), and the methylmethacrylate causes severe pulpal irritation. These cements have been suggested for the cementation of post and cores into endodontically treated teeth where the film thickness and pulpal irritation are not critical factors.

Filled resin cements are currently available for the cementation of acid-etched fixed partial dentures. The resin cement is used to mask the dark color of the metal by the addition of metallic oxide opacifiers.

#### Glass Ionomer

Wilson et al (9) developed glass ionomer cements for permanent cementation and Class V restorations. These cements are combinations of polyacrylic acid liquid and zinc silicate powder (same powder as silicophosphate cement). Although the strength values of this cement are high (as high as zinc phosphate cement), the solubility is also high which mandates concern over the use of this material as either a cement or a Class V restorative material (10).

#### Bases, Liners and Varnishes

Base materials of calcium hydroxide in a disalcylate that sets are packaged in two paste systems (a catalyst and base). Calcium hydroxide is the base of choice under composite resin when a cavity is close to vital pulpal tissue (calcium hydroxide will not inhibit the set of resin materials as do zinc oxide eugenol materials). Calcium

hydroxide, which has a basic pH, can stimulate odontoblastic activity and reparative dentin formation when placed near vital pulpal tissue.

Liner and varnish materials are of two types: copal resins or methyl cellulose in an ether base which evaporates rapidly when exposed to air, and zinc oxide and eugenol in a thin consistency. Liners and varnishes are intended for use in thin layers over exposed dentin surfaces. The high solubility of these materials precludes their use in areas exposed to oral fluids.

The numerous dental cements, cavity liners, and bases challenge the dentist to select the proper material for each specific situation. Cementing cast restorations requires attention to the properties of strength and solubility. Tensile strength is the weakest strength property for all dental cements, and selection of a cement should be made with consideration of an acceptable tensile strength. A dental cement should have reasonable resistance to solubility in oral fluids. Cavity liners and bases should be used in areas where solubility is not relevant, and the thickness of cavity liners and bases must be proportional to their tensile strength. Lining and base materials should be compatible with the restorative material. The dentist must be concerned about the chemical compatibility as well as the medicinal properties of liners and bases.



TABLE 1  
DENTAL CEMENTS AND MANUFACTURERS

Type	Name	Manufacturer
Zinc phosphate	Flicks Tenacin Improved (several shades)	Mizzy, Inc. L.D. Caulk, Inc. S.S. White, Inc.
Silicophosphate	Fluor-Thin Lucent Dorcate	S.S. White, Inc. L.D. Caulk, Inc. L.D. Caulk, Inc.
Polycarboxylate	Durelon P.C.A. Carboset	Premier Dental S.S. White, Inc. Kerr Dental Mfg.
Zinc oxide & eugenol (unreinforced)	Cavitec Temp-bond Cavity Lining	Kerr Dental Mfg. Kerr Dental Mfg. S.S. White, Inc.
Zinc oxide eugenol (reinforced)	Temrex Fynal B & T IRM	Interstate Dental L. D. Caulk, Inc. L. D. Caulk, Inc. L. D. Caulk, Inc.
EBA cements (40% alumina + 60% ethoxybenzoic acid liquid)	Opotow EBA Zebacem	Getz-Teledyne L. D. Caulk, Inc.
Acrylic cements	Grip Justi Resin	L. D. Caulk, Inc. H. D. Justi Co.
Filled resin	EpoxyLite CBA 9080 Resin Bonded- Bridge Cement Comspan	Lee Pharmaceuticals Kerr Inc. L. D. Caulk, Inc.
Glass ionomer	ESPE ASPE  Fuji	ESPE-Premier L. D. Caulk (same material as ESPE) G. C. Corp.
Calcium- hydroxide	Dycal Life	L. D. Caulk, Inc. Kerr Mfg. Co.

TABLE 2  
USES OF DENTAL CEMENTS, BASES, AND LINERS

Product	Use	Advantages	Disadvantages
ZnPO <sub>4</sub>	final cementation & bases	sets hard mixes easily	pulpal irritation
Silico-phosphate	final cementation	high strength	high solubility
ZnOE	temporary cementation & bases	bacteriocidal easily mixed	very high solubility low strength
Reinforced ZnOE	temporary cementation, bases, & temporary restorations	bacteriocidal easily mixed	high solubility low strength
Polycarboxylate	final cementation, & bases	chelation to enamel, pseudoplastic	high solubility low strength short working time
Glass ionomer	final cementation, Class-V restorations	chelation to enamel, fluoride release, high strength	high solubility long setting time
CaOH bases	pulp-capping, & thin bases	stimulates- odontoblastic- activity, easily mixed	very high- solubility, low strength
Resin cements	cement-acid-etched-bridges, & post & cores	good adhesion to enamel, low solubility	high film thickness, pulpal irritation, short working time

TABLE 3  
MANIPULATIVE VARIABLES OF ZINC PHOSPHATE CEMENT

Factor	Effect
Water added to liquid	increased reaction rate (cement sets quicker)
Rapid addition of powder to liquid	increased reaction rate (cement sets quicker)
Mixed cement sets in contact with water	increased cement solubility (formation of highly soluble "hopite crystals")
Cold mixing slab (6 to 26°C)	50% more powder can be incorporated and set of cement prolonged 2-3 times
Frozen slab (-100 to 60°C)	50% more powder can be incorporated, set of cement prolonged 2-3 times; and water condensation is not a problem

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CHAPTER V  
DENTAL PORCELAIN

Porcelain was introduced to the dental profession by M. N. Dubois de Chemant in 1788 as "mineral paste" and was first used to fabricate complete dentures. This early formulation consisted of "Fountainbleau sand" (quartz), alicant soda (sodium carbonate), marl (clay and calcium carbonate), red oxide of iron (pigment), and cobalt (pigment) (1). With the development of the high-heat gas porcelain furnace by Land in the late nineteenth century and the formulation of porcelains with less shrinkage, fabrication of porcelain jacket crowns was possible. The composition of the porcelains used by dentists during this early period varied from dentist to dentist, but the components were essentially the same as those introduced by de Chemant in 1788. In the late 1950s, Weinstein obtained a patent for Permament Porcelain which was the first dental porcelain with a low coefficient of thermal expansion. This low coefficient of thermal expansion porcelain could be matched to the coefficient of thermal expansion of gold based alloys (the first of which was Jelenko-O) which enhanced the bonding of porcelain to metal copings. Previous attempts to bond porcelain to metal substrates resulted in bond failure because of mismatched coefficients of thermal expansion. The Permament patent was sold to the Ceramco Corporation in the early 1960s and became Ceramco porcelain (Johnson & Johnson Co.).

This chapter contains information on the historical background, composition, classification, and bonding of dental porcelain (Table 1). Also, it includes discussions on variations in tooth preparation, suggestions for porcelain manipulation, and descriptions of two new dental porcelain products, "Cerestore" and "Dicore," with some elaboration about their compositional and manipulative differences. A list of common porcelain and ceramic terms appears in (Table 2).

## COMPOSITION OF DENTAL PORCELAIN

The principle components of modern dental porcelain (Table 1) are potassium feldspar (about 80%), silica (about 15%) which is pure quartz, kaolin or clay (5% or less), and fluxes (3% or less). Feldspar is a triaxial combination of potassium, aluminum, and silica. Feldspar fuses easily in temperatures near 1290°C (2354°F) and provides the glassy phase or matrix to the sintered mass of porcelain (2). Silica fuses at high temperatures. Silica is unchanged by the sintering process used on modern dental porcelain and, therefore, it provides the refractory component around which the feldspar fuses. Kaolin or clay is a sticky substance which helps mold the mass of unsintered powders. Kaolin increases the opacity of the sintered mass; and, because it is similar in composition to feldspar, it fuses easily in temperatures near 1290°C (2354°F). Dental porcelains are mixtures of these powders which are produced by first being fused at high temperatures (above 1500°C or 2732°F) producing a mass called a frit. The frit is reground into powder; then, metallic oxides are added which provide the various colors and pigments of the porcelain (3p299).

TABLE 1

## COMPOSITION OF MODERN DENTAL PORCELAIN

Component (%)	Chemical Formula	Function
Feldspar (75-85%)	$K_2O \ Al_2O_3 \ 6SiO_2$	matrix
Kaolin (5% or less) (clay or mullite)	$Al_2O_3 \ 2SiO_2 \ 2H_2O$	holds unsintered mass together
Silica (15%)	$SiO_2$ "crystalline quartz" is used in dental porcelain	refractory
Metallic oxides, kernite, borax, and fluorspar (3% or less)	$Na_2B_4O_7 \ H_2O$ $Na_2B_4O_7 \ 10H_2O$ $CaF_2$	fluxes lower melting range

TABLE 2

## DEFINITIONS AND KEY TERMS OF CERAMICS AND PORCELAIN

Term	Definition
Dental porcelain	(really a glass) a vitreous, amorphous, translucent material composed of fused particles of potash (feldspar) surrounding particles of unfused silica.
Glass	a vitreous, amorphous, translucent or transparent material which has less infusible $\text{SiO}_2$ content than porcelain.
Vitrification	the fusion of porcelain or glass into a transparent or translucent amorphous matrix.
Devitrification	the heating of a glass or porcelain for prolonged periods, to temperatures just below the glass transition temperature, which results in an opaque crystalline mass.
Sintering	the fusion process of powders of porcelain or glass by heating above their glass transition temperatures.
Glass transition temperature ( $T_g$ )	the range of temperatures to which a glass, porcelain, or ceramic must be heated or cooled to change its physical state from a solid to a liquid or from a liquid to a solid.
Frit	fused mass of ingredient powders (prepared by the manufacturer), which when reground will yield porcelain powder

## CLASSIFICATION OF DENTAL PORCELAINS

Modern dental porcelains are traditionally classified by the range of fusion or sintering temperature which they exhibit (4). Sintering is the incremental fusing or coalescing of the porcelain powders. The fusion temperature, also termed the "glass transition temperature" (3p93), is a range of temperatures which is altered slightly each time the mass is refired. When porcelain is heated to temperatures near the glass transition temperature for prolonged periods, the porcelain will devitrify and form opaque crystalline structures (3p300).

## Ultralow-fusing

Ultralow-fusing dental porcelain is composed of sodium silicate or borosilicate glass and fuses in temperatures near 870°C

(1600° F) (5). Ultralow-fusing porcelain is used as stains and glazes on low-fusing porcelain. Surface stains are more easily applied to porcelain surfaces which have a matt finish ("biscuit bake") produced by firing the low-fusing porcelain below the temperature necessary to create a naturally glazed surface, or by roughening the surface with 25 micron alumina or fine diamond stones.

## Low-fusing

This dental porcelain is the "Ceramco-type" porcelain which is fused to metal copings in ceramo-metal restorations and fuses in temperature ranges from 870 to 1066°C (1600 to 1950°F). The source of the porcelain-to-metal bond is from four sources: chemical bonding, slight mismatches in coefficients of thermal expansion, mechanical interlocking, and van der Waals forces.

Chemical bonding occurs through the oxidation of metallic oxides of iron, indium, and tin within the ceramic metal (6). The oxide formation is initiated during the "degassing" procedure and continues by ion diffusion through the last firing. Metals which have a high base metal content or which have been excessively fired, may result in porcelain-metal bond failure because of over-oxidation. The use of gold-flash coatings (Britecoat-Ceramco, Inc) will prevent the contact of silica ions of porcelain and metal oxides within the metal coping. The result is a poor bond.



Slight mismatches in coefficients of thermal expansion enhances bonding (7). When the alloy coefficient of thermal expansion is slightly greater than the porcelain, the porcelain will be held in compression onto the coping surface. If the mismatches in coefficient of thermal expansion are too great, bond failure will result. If the coefficient of thermal expansion of the porcelain is too much lower than that of the metal substrate, the porcelain will crack upon cooling. If the coefficient of thermal expansion of the metal is too much lower than that of the porcelain, the porcelain may fail to contact the metal substrate adequately in critical areas which will result in bond failure, not evident until the porcelain is stressed.

Mechanical interlocking of porcelain into small irregularities of the metal surface can provide some retention (large undercuts in the metal surface will be sources of stress concentration and potential fracture of the porcelain). Studies by Anusavice et al (8) have demonstrated in silver-palladium metals, the presence of surface nodules created by internal oxidation of tin during the "degassing" procedure. These nodules may aid in bonding of porcelain to silver-palladium ceramo-metals.

When two wet surfaces contact, van der Waals forces are present. The polar charge of the wet molecules of opaque porcelain results in van der Waals forces--the weakest of all bonding mechanisms in ceramo-metal bonding.

Low-fusing porcelain is composed principally of potassium feldspar (80%) which contains the high-fusing mineral "lucite" (stable at low-fusing temperatures) responsible for lowering the coefficient of thermal expansion of low-fusing porcelain (9). From the feldspar component, low-fusing porcelain derives the name "feldspathic porcelain." Because all the components of low-fusing porcelain are completely dissolved at the sintering temperature (the components of medium and high-fusing porcelain do not completely dissolve at their fusing temperatures), some authors prefer to call this material a glass (10).

#### Medium-fusing

This porcelain fuses in temperatures from 1090 to 1260°C (2000 to 2300°F). Medium-fusing porcelain has less lucite content in the feldspar which results in a higher coefficient of thermal expansion than low-fusing porcelain. Fluxes are added to low and medium-fusing

porcelains which help to lower their melting temperatures. Medium-fusing porcelain is used in the fabrication of pontic facings and porcelain jacket crowns. In the fabrication of porcelain jacket crowns, platinum foil 0.025 mm thick is folded over a refractory die and sealed to itself with a "tinner's joint" to prevent the porcelain from sticking to the die. Pontic facings are wet formed in molds then sintered. In 1965 McLean and Hughes<sup>11</sup> introduced aluminous core porcelain which has twice the fracture strength of feldspathic porcelain. Aluminous core porcelain is 40% alumina particles added to a medium fusing porcelain. The alumina particles provide strength by preventing propagation of cracks and flaws in the sintered mass of core porcelain (12). This material is not used extensively in the United States but is widely used in Great Britain. The "twin-foil" or "tin-plated" technique, also introduced by McLean and Sced (13), was developed to strengthen the aluminous core. This technique uses two thicknesses of platinum foil. One piece of foil is plated with tin to enhance the bond of aluminous core porcelain to the platinum foil. The second piece of platinum foil serves as a cement spacer and covers only the axial surfaces of the die. The twin-foil technique has failed to achieve significant use in the United States (13).

#### High-fusing

High-fusing porcelain fuses in temperatures of 1280 to 1375°C (2350 to 2500°F). Now, it is used in the fabrication of porcelain denture teeth; in previous years, it was used for porcelain jacket crowns. Because of the sensitive handling properties (easily contaminated by any foreign object), this material is almost exclusively used by dental manufacturers.

Opaque porcelains are formulated by the addition of opacifying metallic oxides to a high, medium, or low-fusing porcelain powder. The opacifying power of dental opaque porcelain is the result of small amounts (5 to 15%) of metallic oxides (zinc oxide, zirconium oxide, and /or tin oxide) which absorb and scatter light (14). The strong opacifying power of dental opaque porcelain diminishes the need to use more than 0.3 mm of opaque porcelain to mask reflective surfaces (15).

All modern dental porcelains, except some glazes, are vacuum fired to increase strength and translucency by elimination of internal voids. Most surface stains and glazes are fired without a vacuum under atmospheric pressure (16).

## TOOTH PREPARATION

Tooth preparation for porcelain jacket crowns and ceramo-metal restorations differ slightly. Tooth preparation for jacket crowns requires a minimum of 1.8 mm overall reduction and at least 2 mm minimum reduction on occlusal surfaces. Although these same guidelines should be followed in tooth preparation for ceramo-metal restorations, the strength and rigidity of the metal coping will withstand slight variations. A modified shoulder or chamfer finish line will increase the space for porcelain, strengthen the restoration, and reduce the effects of stress concentrations in porcelain jacket crowns (17). Porcelain-metal margins are strongest if a beveled shoulder or chamfer is used.

## MANIPULATION OF DENTAL PORCELAIN

Dental porcelain can be ground easily with diamond stones. A smooth surface can be achieved with silicone dioxide stones and abrasive rubber wheels.\* Although auto glazes are considered preferable to topically applied glazes, Noble (Ward Noble, DDS, lecture at the American College of Prosthodontists, October 1974) found that a well-polished porcelain surface was as smooth as a glazed surface. Thompson et al (18) found that hydrofluoric acid in topically applied acidulated phosphofluorides could easily etch glazed porcelain and result in loss of surface gloss in less than 20 minutes. In patients with porcelain restorations, stannous fluoride is less destructive than acidulated phospho-fluoride.

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- \* 1. Shofu Porcelain Polishing Kit, Shofu Dental Corp, 186 Constitution Dr, Menlo Park, CA 94025.
2. Centrix Porcelain Wheels 1-4, Dentsply International, York PA 17405.
3. Dedeco "Niblets" brown rubber points, 3-M Dental Products, St. Paul, MN.

## NEW PORCELAIN PRODUCTS

Two new porcelain restorative materials have been introduced which are products of different aspects of ceramic science. Ceramco Cerestore, marketed by Johnson and Johnson, is an alumina reinforced core material onto which pigmented low-fusing porcelain is fired (19). The core material in this technique is similar to the core material introduced by McLean and Hughes (11), but the core is formed by the extrusion of heat-softened alumina porcelain into a lost-wax refractory mold (20). The source of color in these restorations is from several shades of body porcelain which are fired onto the alumina core. Corning Glass Works and Dentsply International are developing a glass-ceramic material called "Dicore." This material is centrifugally cast into a lost-wax refractory mold of the full contour restoration. The transparent glass restoration is heat-treated and devitrification or ceraming transforms the glass into a ceramic by mica crystallite grain growth. The mica crystallites provide not only translucency to the restoration but strength through a crystalline matrix (21). Dicore ceramic restorations are reported to have twice the fracture strength of feldspathic porcelain restorations. The color or shade of each Dicore restoration is produced by surface application of low-fusing stains and glazes. The final restoration is translucent, hence, the color of the cementing medium requires consideration; whereas, Cerestore and other high alumina core materials are opaque and easily mask highly reflective underlayers.

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## CHAPTER IV

## DENTAL CASTING ALLOYS

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Few metals, with the exception of mercury, gold, and platinum are used in dentistry in their pure form. Not only are pure metals expensive, but also each metallic element possesses unique mechanical and physical properties which may limit the dental application when used in its pure form. For example, although gold is biocompatible and has excellent corrosion resistance, the pure metal is relatively expensive and has low strength properties which precludes its use in stress-bearing areas. In contrast, a less costly metal such as copper, which is not biocompatible and is susceptible to corrosion, may be added in small quantities to gold to enhance the strength properties. For dental purposes, the combination of two or more metals which are generally mutually soluble in the molten condition is defined as an alloy.

This chapter provides information on the different ways alloys are classified, the composition, cost factors, and brief paragraphs on five ceramo-alloys. It concludes with a discussion on the biological considerations of base metal alloys and Type III and IV alloys.

## CLASSIFICATION OF ALLOYS

The metallurgic classification of alloys is relatively clear cut and distinct. On the most simplistic level, alloys can be classified according to the number of alloying elements. If two elements are present, a binary alloy is formed; if three metals are present, a ternary alloy results, and so forth. As the number of elements increases, however, the structure becomes increasingly complex. For dental purposes, alloys may also be

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classified according to the miscibility of the atoms in the solid state. If the atoms of the metals intermingle randomly and the structure is homogenous, such that they resemble a pure metal, and the metals are soluble in each other in the solid state, these alloys are called solid solutions. Most of the dental gold alloys are of the solid-solution type.

With certain alloys, the metals that form solid solutions may not be completely soluble in each other in all proportions. Hence, they may be only partially soluble; and, intermediate phases may develop which are not mutually soluble in the solid state. Alloys which form intermediate phases are further classified metallurgically as eutectic and peritectic alloys.

In contrast to a pure metal, which has a distinct fusion or melting point, most alloys will change from the solid to the liquid phase over a distinct range of temperature. The exception is certain binary alloys in which, at a specific composition, an alloy called a eutectic is formed. A eutectic alloy resembles a pure metal, in that, it will have a distinct fusion point rather than a range of temperature. A eutectic composition of 71.9% silver and 28.1% copper, will form at a melting point of 779.4°C which is lower than the melting points of either silver or copper. Because of the presence of insoluble phases which inhibit grain slip, the strength and sometimes the hardness of these alloys surpasses that of the constituent metals. As discussed in the Dental Amalgam chapter, the silver-copper eutectic is an important component of current admixed high copper amalgam alloys. Except for this application and certain gold solders, the eutectic systems generally are not used in casting alloys because of their low tarnish and corrosion resistance.

In the chemical classification, certain metals in the periodic table of elements are considered "noble." These include gold, silver, platinum, and the platinum group metals (palladium, rhodium, ruthenium, iridium and osmium). Major metallurgical societies and federal governmental agencies, such as the National Bureau of Standards, also consider these metals to be "precious." On this basis, a dental alloy which contained no gold, but only silver, platinum and palladium, might legitimately be termed a precious or noble alloy. Nobility also carries with it the connotation of resistance to tarnish and corrosion. Although three of the noble metals - gold, platinum, and palladium - are relatively inert, anyone who has polished sterling silver (92.5% silver) is aware that



this noble metal is easily tarnished. Therefore, it is possible to formulate a noble or precious alloy which is not inert in the oral cavity.

#### COMPOSITION OF ALLOYS

Historically, casting gold alloys contained a minimum of 75 to 83% gold and platinum-group metals to preserve their resistance to tarnish and corrosion. In 1968, the United States government placed the price of gold on the free market. Since that time, the steady increase in the cost of this metal has prompted the development and expanded utilization of less expensive alternative alloys. The reduction in cost has been achieved by substituting other metals which either decrease or completely eliminate the precious elements. As the gold content of the current casting alloys decreased below these levels, a confusing nomenclature evolved; these alloys have been called white golds, yellow golds, precious, semi-precious, non-precious, high noble, medium noble, low noble, high gold, medium gold, low gold, base metal and other imprecise terms such as "economy" alloys.

Since 1977, the American Dental Association has required dental alloy manufacturers to specify the percentage of gold, platinum and palladium in their alloys. Unfortunately, the requirements pertain only to those manufacturers who voluntarily elect to participate in the ADA's certification or acceptance program. Therefore, it is the practitioner's responsibility to obtain the composition of the alloy from the manufacturer.

Composition may be expressed in percentage or parts per 100 of the metals used in the alloy. Casting gold alloys and solders also may be characterized according to "fineness" or "karat." The fineness of a gold alloy is the parts per thousand of pure gold. Pure gold is 1000 fine. An alloy composed of three-fourths of pure gold is said to be 750 fine. The karat of an alloy is the parts of pure gold in 24 parts of alloy. For example, 24 karat gold is pure gold, and 18 karat gold contains 18 parts pure gold and 6 parts of other metals. Therefore, it is possible to describe an alloy with the same composition as 750 fine, 18 karat, or 75 percent gold.

Current alloys may contain no gold, or as little as 2%, or up to a maximum of 90.5% gold. Although the Federal Trade Commission for the jewelry industry states that an alloy must contain more than 41.6 weight percent gold to be termed a gold-based alloy, no such standards apply to dental alloys. In fact, several alloys, containing as little as 2% gold, have "gold" included in the brand name.

#### COST FACTORS

Precious metal alloys are sold on the basis of cost per unit weight such as dollars per ounce or dollars per pennyweight. To compare the relative economy of one alternative alloy to another on the basis of cost per unit weight alone can be misleading, especially if there is a significant difference between the densities of the two alternatives. A greater number of castings can be produced by a less dense alloy. Therefore, a realistic comparison of the relative cost of several alternative alloy selections should be on the basis of dollars per cubic centimeter (cc), rather than dollars per ounce. In order to calculate the cost of a candidate alloy, I suggest using the following formula:

Dollar Cost per cc = (Dollar Cost per Ounce) X (Density of Alloy)

31.10486

In light of the absence of applicable compositional standards which manufacturers are obliged to follow, the following classification of alternative alloys will be based upon their utility and principal metals contained in each ceramo-alloy:

Gold-platinum-palladium  
Gold-palladium-silver  
Gold-palladium  
Palladium-silver  
Base metal

## CERAMO-ALLOYS

The increased emphasis upon esthetic dentistry has resulted in more activity in the development of alloys, which are intended as substrates for fused porcelain veneers, than any other type of alloy. These alloys have also been referred to as metal-ceramic alloys and porcelain-fused-to-metal (PFM) alloys. It must be recognized that the overlying porcelain veneer is a brittle material which is fired at relatively high temperatures. This places stringent metallurgic demands upon this type of alloy. In addition to the biologic and corrosion resistance requirements which are common to all alloys, the presence of porcelain requires that there be a compatibility between the thermal expansion characteristic of the porcelain and the alloy to resist cracking, crazing and fracture of the alloy-porcelain bond. In view of the relatively high temperature achieved during the firing of the porcelain, the alloy should be sag resistant at these temperatures. Flexure of an alloy substructure beneath a brittle ceramic would result in fracture of the porcelain. Therefore the alloy should be rigid. Lastly, since esthetics is a matter of high priority, there should be no pigmented reaction produced between the porcelain and the alloy.

## Gold-platinum-palladium Alloys

These alloys contain between 80 and 90% gold, and they represent a type of alloy with the longest history of clinical efficacy. The high gold content imparts excellent tarnish and corrosion resistance, familiar handling characteristics (casting, grinding, soldering, polishing) and a gold color which minimizes esthetic complications, especially in anterior restorations. The majority of these alloys contain either no or minimal amounts of silver -- a factor which also contributes to the improved esthetics of the final restoration. In order to achieve rigidity of the metal substructure, adequate thickness of connective areas must be maintained. Because of the high percentage of gold and platinum in these alloys, a relatively high material cost is a disadvantage. Platinum and gold have the highest density of the four precious metals. With densities ranging from 17.5 to 18.5, fewer castings per unit weight may be produced with these alloys. In addition, the cost per unit weight is the highest of the ceramo-metals. Another disadvantage is the tendency for these alloys to sag or deform under their own weight unless they are supported during the porcelain firing procedure.

### Gold-palladium-silver Alloys

The gold content of these gold-palladium-silver ceramo-alloys is within a broad range of 40 to 75% with some alloys as low as 16%. In view of their relatively low gold content, the majority of these alloys are "white" colored. Their density and relative cost are less than the gold-platinum-palladium alloys. They possess greater rigidity and sag resistance; thus they can be used to make longer span bridges. However, there is a tendency for these alloys to discolor the porcelain because of the silver content.

### Gold-palladium Alloys

To prevent porcelain discoloration caused by the presence of silver, the gold-palladium ceramo-alloy was produced. It is a white alloy containing no silver; the melting range is higher because of the palladium content; and it has less chance of thermally induced sag. Although it is a harder and stronger alloy, the manipulation characteristics, such as casting, soldering, grinding and polishing, are similar to the gold-platinum-palladium alloys. These factors contribute to its usefulness in longer span bridges. Coupled with its excellent tarnish and corrosion resistance, this alloy combines all of the advantages of the other alloy types with none of the disadvantages.

### Palladium-silver Alloys

The palladium-silver ceramo-alloy contains no gold and the palladium content can range from 50 to 60% with a silver content of 30 to 40%. Without the most costly and dense element (gold), this alloy is the lowest cost ceramo-alloy discussed in this chapter. The physical properties of this alloy are comparable to the others. A major problem associated with the relatively high silver content is the strong tendency to produce a green discoloration in porcelain, especially in the lighter shades. It should also be recognized that contamination of the porcelain chamber walls and the saggar trays with silver is a real problem. Periodic decontamination of the chamber by use of a graphite block is recommended.

### Base metal Alloys

The distinguishing feature of base metal ceramo-alloys is that they do not contain noble metals and the term

'nonprecious' is an appropriate description. The majority of these alloys are nickel-chromium-containing materials in which the nickel content may range from 70 to 80%, while the chromium may vary between 13 and 20%. Other base metal formulations are based upon cobalt-chromium in which the cobalt content is approximately 65 and the chromium approximately 25%.

The lack of precious metals, the relatively low material cost of component elements and their low density make the base metal alloys the least expensive of the ceramo-alloys. In general, the mechanical properties of these alloys offer significant advantages over the other ceramo-alloys (1). They possess a rigidity (modulus of elasticity) and resistance to permanent bending (yield strength) which is more than twice the rigidity and resistance of other alloys. In addition, their high melting temperature contribute to the alloys' excellent resistance to sag at the elevated porcelain firing temperatures (2). These factors enhance the application of base metal alloys for use in long span bridges.

Approximately 66% of surveyed laboratories were using base metal alloys in 1980 (3). This is a significant increase over the usage in 1979 which was only 37%. Apparently, with the increasing popularity of base metal, and the less costly silver-palladium precious alloy, the use of the gold-platinum-palladium and gold-palladium alloys has declined. Although some persons claim that these base metal alloys are "technique sensitive," this same survey (3) showed that greater than 90% of the laboratories expressed satisfaction with casting the alloys, the low incidence of bubbles in the porcelain and the need for remakes, and the adequacy of the porcelain-metal bond. Only soldering remained a problem for 35% of the laboratories surveyed (3).

From a clinical standpoint, the high hardness and extremely low ductility (especially the cobalt-chromium alloys) are matters of concern (4). High hardness contributes to excellent wear resistance, but this property also makes it difficult to perform occlusal adjustments and repolish the adjusted areas. The sectioning and removal of defective restorations can also be a time-consuming procedure. The low ductility means that the alloys cannot be burnished to perfect minor marginal discrepancies--another disadvantage which places greater emphasis upon the need for casting accuracy.

## BIOLOGICAL CONSIDERATIONS OF BASE METAL ALLOYS

Certain of the base metal alloys contain beryllium which is added to the alloy to reduce the fusion temperature, improve the casting characteristics, refine the grain structure, and possibly participate in the bonding of porcelain (5). Beryllium-containing alloys perform better than other alloys when employed with the etched metal resin-bonded cast restoration technique. To date, there have been no documented cases of beryllium toxicity of dental origin. However, under uncontrolled conditions, where inhalation of dust and fumes may be anticipated, the presence of beryllium constitutes a recognized health hazard. Therefore, where grinding of beryllium-containing alloys is performed, adequate local exhaust ventilation safeguards should be used.

Epidemiologic studies on workers in non-dental industries have implicated nickel and nickel compounds as carcinogens (6). The major hazardous route is by aspiration. No experimental evidence indicates that nickel compounds are carcinogenic when administered by oral or cutaneous routes. Since nickel-chromium alloys can contain up to 80% nickel, the prudent course of action is to take precautions to prevent the aspiration of nickel-containing dust produced during grinding operations.

Nickel is a potent sensitizing agent and it produces more instances of contact dermatitis than all other metals combined. Patients who are allergic to nickel will also react to certain nickel-chromium dental alloys (7). There is a significant difference in the incidence of nickel sensitivity between males and females. A recent study (8) has shown that between the ages of 24 and 44, 9.7% of female dental patients were sensitive to nickel as compared to only 0.8% of the males. The relative risk of female sensitivity within this age group was 4.8 times that of other age groups. Female patients with pierced ears were also more likely to be sensitive to nickel. However, it was interesting to note that the intra-oral exposure to nickel-containing dental alloys did not result in an increased incidence of nickel sensitivity. In view of the available evidence, it is the dentist's responsibility to take a careful health history with particular emphasis upon sensitivity to metals and the incidence of pierced ears and jewelry related dermatologic symptoms. The intra-oral use of nickel-containing dental alloys is contraindicated in nickel-sensitive individuals.

## TYPE III AND IV ALLOYS

The American Dental Association Specification Number 5 for Type III and IV alloys requires a minimum content of gold and platinum group metals between 75 and 78 percent. These are the alloys which are used for fixed prosthodontic applications (without porcelain veneers). The relatively high noble metal content was selected because alloys below 65 to 75% tarnished too rapidly for use in the oral cavity.

In a recent survey of dental casting alloys (9), 80% of the alloys did not comply with the ADA specification. These alloys have noble metal contents which fall below the accepted levels and are not either certified or accepted. The least costly alloys contain approximately 70% silver and 25% palladium. Although silver can tarnish within the oral cavity, the addition of palladium significantly increases the tarnish resistance and serves to harden the alloy. The addition of gold also allows these alloys to be age hardened. The casting of certain of these alloys is more difficult than the traditional gold alloys. In view of their relatively brief clinical history, their resistance to tarnish and corrosion has yet to be proven.

The diversity of alloys available to the dental practitioner has never been more extensive than at the current time. We now have the opportunity to select alloys based upon the individual patient's specific biological, functional, and economic requirements. There is no one alloy which is suitable for all applications, since in metallurgy there is a constant trade-off in properties as changes in formulations are made. To make optimum utilization of the choices available and for obvious ethical and medico-legal considerations, it is incumbent upon the practitioner to be aware of the identity and composition of the alloy he prescribes.

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## CHAPTER VII

## ELASTIC IMPRESSION MATERIALS

In the past one hundred years, dentistry has advanced tremendously. One of the hallmarks of this advancement, has been the ability to fabricate restorations indirectly in a controlled dental laboratory environment. Fifty years ago, fabrication of wax patterns for cast restorations was performed directly in the patient's mouth. Conversely, dentures could be constructed indirectly on casts made from sectional plaster impressions. The invention of agar hydrocolloid by Alphons Polar and its adaptation by Sears for indirect wax patterns fabrication marked a new era in restorative dentistry (lp225).

This chapter contains information about two main categories of elastic impression materials and their uses--hydrocolloids and nonaqueous elastomeric impression materials. Tables 1 and 2 are provided to enumerate the product names and manufacturers of the elastic impression materials. Table 3 lists the main properties of the seven most common types of elastic impression materials.

## HYDROCOLLOID IMPRESSION MATERIALS

## Agar Hydrocolloid

In 1926 Alphons Polar patented agar impression material. It was marketed by the DeTrey Co. as "Denticole." Sears is credited with the adaptation of its use from a denture impression material to use for cast restorations (lp226). Agar impression material (also called "agar-agar" and "reversible hydrocolloid") is a reversibly thermoplastic material made from two types of red algae (gelidium and gracilaria). Because the material is a colloidal suspension of particles of algae in water, the material is hydrophillic; and making an impression of a wet surface is not a problem. Agar hydrocolloid requires the use of special equipment to heat the material to liquid consistency and must be cooled in the patient's mouth by

using special hoses and water cooled trays. Boiling in a water bath is necessary for agar hydrocolloid to be altered physically from a gel (solid) to a sol (fluid). The solidification (gelation) temperature of agar hydrocolloid is different from the liquification temperature by 40 to 50°F (5 to 10°C), a property called "hysteresis." Hysteresis of agar hydrocolloid yields excellent handling characteristics because the material can be used in an injectable form at 145°F (45°C) and it will solidify at a point slightly above body temperature (100°F or 37°C). The borax which is added to increase the strength of the agar hydrocolloid also retards the normal setting reaction of dental stone. Therefore, the surface of the agar should be sprayed with a 2% solution of potassium sulfate which is an accelerator of the setting reaction of dental stone. Most modern agar impression materials contain potassium sulfate, but a simple spray of the impression with the 2% potassium sulfate solution will insure that all areas of the cast will set properly (2).

#### Alginate

Before 1938, the principal source of algae used in the fabrication of agar hydrocolloid was from the Far East. During World War II, a critical need for a nonrigid impression material surfaced when the supply of algae from Far East Asia was interrupted. This need was met by an impression material developed in England by Wilding in 1940 (3). The artificial agar hydrocolloid or alginate was a mixture of sea weed (diatomaceous earth) and plaster of Paris. When mixed with water, alginate or irreversible hydrocolloid reacts chemically to form an elastic material with properties similar to agar hydrocolloid. Alginates used in modern dentistry have been improved tremendously over the last forty years, and the dimensional accuracy of this impression material is close to that of agar hydrocolloid, but its ability to reproduce fine detail is much inferior. The material preparation and ease of handling of alginate have popularized its use for restorative procedures where fine detail reproduction is not essential. High water/powder ratio prolongs the setting time, and increased spatulation accelerates the setting time of alginate impression materials. Craig et al (4) have reported that alginate materials can be stored in an environment of 100% humidity for up to one hour without any significant effect upon the accuracy of the impression. If not protected from desiccation, agar hydrocolloid and alginate impression materials are susceptible to dehydration also called syneresis. If either material is emersed in water for prolonged periods of time, it will

imbibe water, a property called imbibition. The filler material in alginate (diatomaceous earth) has been linked with respiratory disease. Inhalation of these fine particles should be avoided (5).

#### Agar/Alginate

The Japanese have developed two agar hydrocolloids which will bond to alginate (Colloid 80 and Dentloid). These materials eliminate the need for preparation and storage of agar hydrocolloid tray material. The new agar hydrocolloids are syringe materials which must be boiled to reach a fluid consistency, but alginate impression material can be used as tray material which simplifies the impression procedure. The care and handling of the combination impression is similar to that of other hydrocolloid impressions and the accuracy of the cast from this material is equal to that of agar hydrocolloid (6).

TABLE 1

#### HYDROCOLLOID IMPRESSION MATERIALS

Material Type	Brand Name	Manufacturer
<u>Agar hydrocolloid</u>		
	Agarloid	Cadco Products
	Altoid	Van R Dental Prod.
	Rubberloid	Van R Dental Prod.
	Surgident	Lactona Corp.
<u>Alginates</u>		
	Coe Alginate	Coe Labs
	Jeltrate	L.D. Caulk
	Kerr Alginate	Kerr/Sybron
	Alginate	S.S. White Co.
	Surgident-	
	Alginate	Lactona Corp.
	Unijel II	Unitek Corp.
<u>Combination</u>		
<u>Agar/alginate</u>		
	Colloid 80	U.S. Shiza Corp.
	Dentloid	Denterials, Ltd.

## NONAQUEOUS ELASTOMERIC IMPRESSION MATERIALS

Elastomeric impression materials have more elasticity and higher tear strength than hydrocolloid impression materials. Each of the elastomeric materials has a chemical setting reaction which results in a rubber-like quality in the impression and permits repouring of some of the materials in this category. Most of these materials are marketed as two-paste systems, although some manufacturers of silicones provide putty/liquid systems for clinicians who prefer a rigid tray material.

## Polysulfide (Rubber-base)

Polysulfide rubber material is provided as a two-paste system in three consistencies; heavy-bodied, medium-bodied, and light-bodied material. One paste contains free sulf-hydral (mercaptain) groups which react with the aid of a second paste containing lead dioxide accelerator, sulfur, dibutylphthalate, and steric acid to form a crosslinked polymer rubber. This reaction can be accelerated with moisture or heat. Polysulfide has the highest tear resistance of all elastic impression materials but, because of its viscoelasticity, polysulfide is the most easily distorted impression material when not stored properly in an upright position. Because of the elastic recovery of polysulfide and the delayed setting reaction of the material, a polysulfide impression must be allowed at least 30 minutes to polymerize and recover from the distortion of removal from the mouth. The accuracy of a polysulfide impression after several hours is less than its accuracy after 30 minutes because the impression will flow with time (viscous component of its viscoelastic character). With time, the viscous flow of the set material will yield dies which would be shorter and fatter than dies from the same impression poured within the first hour (7). Even though polysulfide has the longest working and setting times of all elastic impression materials and is the least expensive elastomeric impression material, the offensive sulfur-odor and clothes staining property have diminished its use by some practitioners.

## Condensation Silicone

This impression material is used least of all elastic impression materials. The one-hour dimensional accuracy of the material is the poorest of all impression materials, and the setting reaction liberates ethyl alcohol and hydrogen gas which can potentially contaminate the surface

of dental stone poured into an impression of condensation silicone.

#### Addition Silicone (Polyvinylsiloxane)

Addition silicone is a design improvement in the basic polymer chemistry of condensation silicone (8). Addition silicone has none of the condensation by-products of condensation silicone and addition silicone has the greatest accuracy of all impression materials. This material is supplied as either a two-paste system with three different consistencies (light, medium, and heavy), or a putty/liquid. The base material of addition silicone contains a silane polymer and chloroplatinic acid catalyst. Addition silicone has less working time and sets more rapidly than polysulfide rubber impression material. Silicones (both condensation and addition) are hydrophobic. To make a good impression with silicone, the oral field must be very dry. The hydrophobic nature of silicone increases the incidence of surface bubbles in the dental cast, but surfactants (Almore Co.) sprayed into the impression will reduce the incidence of surface bubbles in the dental stone (9).

#### Polyether

Polyether impression material was developed before addition silicone. If addition silicone had appeared first on the market, polyether might never have been developed. All of the properties of polyether are either similar to or less than addition silicone; furthermore, polyether is the most expensive dental impression material. Polyether impressions are the stiffest of all elastic impression materials, a property which can result in broken teeth on a stone cast. The working and setting times of polyether are the shortest of all elastic impression materials. Clearly, the advantage of this material over all other elastic impression materials is its possible use as an interocclusal record medium. Polyether is supplied as a paste/paste system in only one consistency. The base material is a polyether, and the catalyst contains a crosslinking agent. The mixed material is a crosslinked rubber polyether polymer (10).

## NEW DENTAL PRODUCTS

## Express

The 3M company has introduced a gun-syringe delivery system which mixes addition silicone as it is expressed from the gun-syringe. The hand-held device is loaded with unmixed addition silicone prepackaged in separate tubes which join into a single syringe tip. As the gun-syringe is squeezed, the material is mixed in the joined tip. This system eliminates the need for an impression syringe. Less time is needed for mixing which is performed within the gun-syringe. This new system is called "Express," and is marketed by 3M Dental Products.

## J Gun

Rasmussen has patented a syringe-gun which can (according to the manufacturer) help make impressions under water. This system is suggested for use with polysulfide rubber impression material. The syringe-gun is connected to a 4, 3, or 2-hole air hose for a handpiece with 45-60 lb of air pressure. Concentric tubes allow the impression material to be expressed from an inner tube and, selectively, the operator may blow air from an outer tube to eliminate water or saliva from the path of the impression material. This system eliminates the need for an air syringe to blow fluids away from the impression area, or the need to blow the impression material (which is hydrophobic) around teeth and into gingival crevices. This system, as claimed by the manufacturer, eliminates the need for gingival retraction cord. This system would be contraindicated for use on teeth with narrow deep gingival pockets in which impression material might be blown and trapped in the gingival pocket creating further problems. The J Gun is marketed by JDR Instruments Inc.

TABLE 2

## NONAQUEOUS ELASTOMERIC IMPRESSION MATERIALS

Type of Material	Brand Name	Manufacturer
<u>Polysulfides (rubber-base)</u>		
	Coe-flex	Coe Labs.
	Permlastic	Kerr/Sybron
	Omniflex	Coe Labs.
<u>Condensation silicones</u>		
	Accoe	Coe Labs.
	Citricon	Kerr/Sybron
	Optosil-	Unitek Inc
	Zantopren	Unitek Inc
<u>Addition silicones</u>		
Products	Cinch-vynal	Parkell Products
	Exaflex	G.C. Inter.
	Express	3M Dental
	Healthco PVS	Healthco Inc.
	Improgel	Healthco Inc.
	Methigum	Dental Materials Group Ltd.
	Mirror 3	Kerr/Sybron
	President	Coltene Co.
	Reflect	Kerr/Sybron
	Reposil	L.D.Caulk Co.
<u>Polyether</u>		
	Impregum	Premier-ESPE
	Permadyne	Premier-ESPE
	Ramitec	Premier-ESPE
	Polyjel	L.D. Caulk Co.

TABLE 3

## PROPERTIES OF ELASTIC DENTAL IMPRESSION MATERIALS

Material	Working-time (min)	Setting-time (min)	Shrinkage (%)	Price/Arch (dollars)
<u>Alginate</u>	3	3.5	0.2* **	0.65
<u>Agar</u>	2	5	0.2	1.25
<u>Agar/alginate</u>	2	4	0.2	1.65
<u>Polysulfide</u>	5	11	0.25	3.00
<u>Silicone</u> (condensation)	4	8	0.56	3.80
<u>Silicone</u> (addition)	5.5	11.5	0.05	5.50
<u>Polyether</u>	3	7	0.09	5.80

\* Shrinkage of hydrocolloid materials is dependent upon the storage conditions of the impression and relative amount of syneresis and imbibition acting upon the material.

\*\* The shrinkage of alginate impression material is in the range considered adequate for cast restorations, but the fine detail reproduction of alginate is not within the acceptable limits needed for accurately fitting cast restorations.



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## NOTES



## APPENDIX A

## DENTAL MATERIALS REVIEW QUESTIONS

The answers to the following questions are found within the text of this syllabus.

1. There are several phases in dental amalgam which were identified by Marie Gayler. Of these phases, which is the most damaging to the set amalgam?
2. There are several different morphological types of dental amalgam. How do the manipulative properties of each differ?
3. How does the "dispersion phase" of modern dental amalgams function as reported by the developer? Does it really function in this manner?
4. What are the differences between "conventional amalgam," "lathe-cut amalgam," "spherical amalgam," "low-copper amalgam," and "high-copper amalgam"?
5. How does an "admix amalgam alloy" differ from a "unicompositional amalgam alloy"?
6. What is the effect of overtrituration of both conventional and high-copper amalgams?
7. What is the "eight-minute polish", and with which amalgam alloys can it best be used?
8. What distinguishes a "fully filled" composite resin material from a "microfilled" composite resin material?
9. What are the advantages of visible-light-cured composite resin over UV-activated composite resin?
10. What bases and cavity liners are best used under composite resin restorations? What will the liners and bases not recommended for use with composites do to the resin material?

11. When using composite resin restorations, when is acid etching essential?
12. Which type of resin restorative material (unfilled, conventional, or microfilled) has the highest modulus of elasticity? Which type of resin restorative material would you chose for a load-bearing area?
13. Which type of resin restorative material is the most color stable? Which resin material is most difficult to finish?
14. How much difference in dimensional accuracy is there between
  - a. Polysulfide and addition silicone?
  - b. Reversible hydrocolloid and addition silicone?
  - c. Addition silicone and polyether?
  - d. Conventional silicone and addition silicone?
15. How does the dimensional accuracy of addition silicone compare to conventional silicone after 24 hours?
16. With which type of ceramic alloy is greening a problem? Why?
17. How does the finishing and polishing of base metal alloys compare to...
  - a. ceramic metals containing a high gold content?
  - b. silver-palladium alloys?
18. What bond problems can be experienced when using base metal alloys? What esthetic problems?
19. Compare the density and reusability of base metal alloys and gold based alloys.
20. Why should the coefficient of thermal expansion of ceramo-alloys used with porcelain be slightly lower than the porcelain of the same system?
21. There are three main components in dental porcelain, what is the chemical element common to all three?
23. If the surface glaze of a porcelain restoration is broken, what can happen if this area is in occlusion (both to the porcelain and the opposing occlusion)? What can be done to correct this problem in the dental operator?

24. If one considers tensile strength, compressive strength, and solubility, what type of dental cement would you use to cement a full crown restoration? Why?
25. How does the cold slab and frozen slab technique affect the setting time of zinc phosphate cement before it is inserted into the mouth?
26. In a patient with high caries incidence, what cement would you choose where solubility is not a great concern?
27. Reportedly, chelation with enamel occurs with what two types of dental cements? What ions are involved?
28. How can the setting reaction of zinc oxide eugenol cement be accelerated?
29. Why is the slow mixing of zinc phosphate cement necessary?
30. How will the addition of water to the liquid component of zinc phosphate cement affect the setting time?
31. To what does the term "slaking" refer, and what dental material can best benefit from its use?
32. When metal is strain-hardened or cold-worked, what might be the effect upon the...
  - a) proportional limit?
  - b) the modulus of elasticity?
  - c) the ultimate tensile strength?
33. What metal is considered by many to be a precious metal but not a noble metal?
34. What karat would a gold alloy be if its gold content were 75%?
35. How is the tensile strength of most brittle materials measured (with what kind of force)?
36. ADA solubility tests are often criticized because of the type of solution into which the samples to be tested are placed; what is the solution?
37. If a gold solder was known to have 75% gold alloy, what would be its "fine" value?

38. What is a eutectic alloy; what is an example commonly used in pedodontics?
39. Two colors are said to be metameres. What are the potential hazards of their presence; what dental materials could exhibit this property, and what can you as a clinician do to prevent their detrimental effects?
40. What is a creep compliance curve, and what dental materials could be characterized by this property?

## APPENDIX B

## MANUFACTURERS' ADDRESSES AND TELEPHONE NUMBERS

The dental products and manufacturers listed in this syllabus are neither endorsed nor suggested for use by the United States Army. This list is presented as an example of some of the dental products available. The reader can find a more thorough listing of dental manufacturers and products by consulting "Dental Products", a list of accepted and certified dental products compiled by the Council on Dental Materials, Instruments, and Equipment and the Council on Dental Therapeutics of the American Dental Association; which is published each November in the Journal of the American Dental Association.

Almore International Inc.  
Box 25214  
Portland, OR 97225  
(800) 547-1511  
(503) 643-6633

Harry J. Bosworth Co.  
7227 N. Hamlin Ave.  
Skokie, IL 60076  
(312) 679-3400

Ash/Densply  
(previously DeTrey)  
324 Chestnut St.  
Box 952  
Toledo, OH 43697  
(419) 241-8039

Cadco Products  
8890 Regent St.  
Los Angeles, CA 90034  
(213) 204-1203

Baker Dental (Div. of  
Engelhard Industries)  
700 Blair Rd  
Careret, NJ 07008  
(800) 631-5599  
(201) 321-5800

Ceramco Inc.  
c/o Johnson & Johnson Co.  
Dental Products Division  
20 Lake Dr.  
East Windsor, NJ 08520  
(800) 257-9508  
(800) 792-8688 (NJ only)  
(609) 443-3300

Coe Laboratories, Inc.

3737 W. 127th St.  
Chicago, IL 60658  
(customer service)  
(800) 323-7063  
(800) 323-3386 (watts)  
(312) 568-2100

Coltene Inc.

14 Kane Industrial Dr.  
Hudson, MA 01749  
(800) 225-9382  
(800) 762-9760 (MA only)  
(617) 562-3881

L.D. Caulk Co.

Box 359  
Milford, DE 19963  
(800) 441-8448 (not in DE)  
(302) 422-4511

Densply International, Inc.

570 W. College Ave.  
York, PA 17405  
(717) 845-7511

Denterials, Ltd.

Box 22037  
St. Louis, MO 63126  
(800) 325-3056 (not in MO)  
(314) 842-4355

Dental Materials Group Ltd.

(Methigum addition silicone)  
150 Broad Hollow Rd.  
Box 1167  
Melville, NY 11747  
(516) 692-4353

Den-Mat Corp.

Box 1729  
Santa Maria, CA 93456  
(800) 235-2441  
(800) 482-4914 (CA)  
(805) 922-8491

ESPE-Premier Sales Corp.

1710 Romano Dr.  
Norristown, PA 19401  
(800) 233-3201 (tech info)  
(215) 277-3800

G.C. International Corp.

8096 N. 85th Way #100  
Scottsdale, AZ 85258  
(602) 948-5854

Getz/Teledyne Densco

3840 Forest St.  
Denver, CO 80207  
(303) 399-0240

Healthco, Inc.

25 Stuart St.  
Boston, MA 02116  
(800) 225-2360  
(617) 423-6045

Interstate Dental Co., Inc.  
(Temrex Division)

112 Albany Ave.  
Box 182  
Freeport, NY 11520  
(516) 868-6221  
(213) 227-8405 (CA only)

JDR Instruments Inc.

1616 North Laurel Ave.  
Upland, CA 91786  
(714) 982-8891

J.F. Jelenko & Co.

99 Business Park Dr.  
Armonk, NY 10504  
(800) 431-1785  
(914) 273-8600

Johnson & Johnson

Dental Products Division  
20 Lake Dr.  
East Windsor, NJ 08520  
(800) 257-9508  
(800) 792-8688 (NJ only)  
(609) 443-3300



H.D. Justi Co.

Div. of Am. Tooth Mfg. Co.  
2233 Straham Blvd.  
Oxnard, CA 93033  
(800) 239-4639  
(805) 487-9868

Kerr Mfg. Div./Sybron Corp.

28200 Wick Rd.  
Romulus, MI 48174  
(800) 521-2854/5  
(313) 946-7800

Litton Dental Products

1001 W. US 56 Highway  
Olath, KS 66061  
(913) 782-2200

Lactona Corp. (subsidiary of  
Warner-Lambert Co.)

Academy & Red Lion Rds.  
Philadelphia, PA 19114  
(800) 523-2559  
(215) 368-2000

Lee Pharmaceuticals

Box 3836  
14444 Santa Anita Ave.  
South El Monte, CA 91733  
(800) 423-4173  
(213) 442-3141  
(collect from CA, HI, & AK)

3M CO. Dental Products

3M Center  
225-5 South  
St. Paul, MN 55101  
(612) 733-8238 (collect)

Mizzy, Inc.

Box 631  
Clifton Forge, VA 24422  
(703) 862-4151

J.M.Ney Co.

Ney Industrial Park  
Bloomfield, CT 06002  
(800) 243-1942  
(203) 242-2281

Parkell Products, Inc.

155 Schmidt Blvd  
Farmingdale, NY 11735  
(516) 249-1134

Phasealloy Inc.

1050 Greenfield Ave.  
El Cajon, CA 92021  
(800) 854-6641  
(619) 440-4633

Premier-ESPE

1710 Romano Dr.  
Norristown, PA 19401  
(800) 233-3201 (tech info)  
(215) 277-3800

Shofu Dental Corp.

4025 Bohannon Dr.  
Menlo Park, CA 94025  
(415) 324-0085

U.S. Shiza Corp.

12418 Santa Monica Blvd.  
Los Angeles, CA 90025  
(213) 820-7710

Star Dental Inc. (subsidiary  
Syntex Dental Products)

Box 896  
Valley Forge Corporate Center  
Valley Forge, PA 19482  
(215) 666-9050

Unitek Corp.

2724 S. Peck Rd.  
Monrovia, CA 91016  
(800) 423-3748 (Dental)  
(800) 423-4318 (Laboratory)  
(800) 423-4588 (Orthodontics)  
(213) 445-7960 (CA collect)

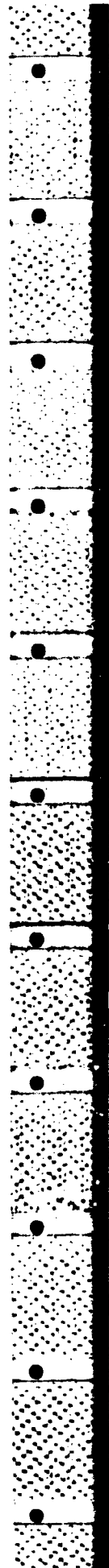
Van R Dental Products, Inc.

8894 Regent St.  
Los Angeles, CA 90034  
(800) 421-0782  
(213) 204-1200 (CA collect)

S.S. White Dental Products Int'l  
Three Parkway, Rm. 800  
Philadelphia, PA 19102  
(215) 587-7401  
(215) 587-7000

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